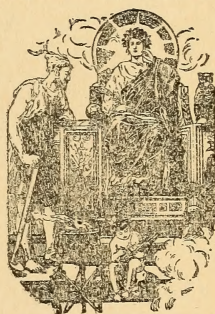


554

SCIENTIFIC LIBRARY



UNITED STATES PATENT OFFICE

GOVERNMENT PRINTING OFFICE

11-8925

2

88808
Int

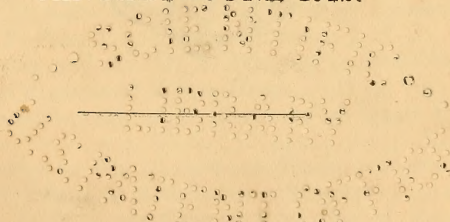
THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

5-1

CONDUCTED BY
SIR OLIVER JOSEPH LODGE, D.Sc., LL.D., F.R.S.
SIR JOSEPH JOHN THOMSON, M.A., Sc.D., LL.D., F.R.S.
JOHN JOLY, M.A., D.Sc., F.R.S., F.G.S.
GEORGE CAREY FOSTER, B.A., LL.D., F.R.S.
AND
WILLIAM FRANCIS, F.L.S.

"Nec araneorum sane textus ideo melior quia ex se fila gignunt, nec noster
vilior quia ex alienis libamus ut apes." JUST. LIPS. *Polit. lib. i. cap. 1.* Not.

VOL. XXIII.—SIXTH SERIES.
JANUARY—JUNE 1912.



LONDON:

TAYLOR AND FRANCIS, RED LION COURT, FLEET STREET.

SOLD BY SIMPKIN, MARSHALL, HAMILTON, KENT, AND CO., LD.
SMITH AND SON, GLASGOW;—HODGES, FIGGIS, AND CO., DUBLIN;
VEUVE J. BOYVEAU, PARIS;—AND ASHER AND CO., BERLIN.

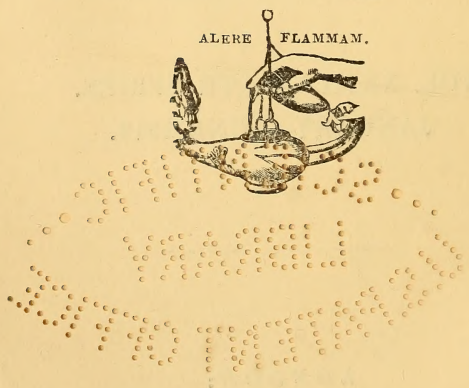
95474

Q
1
P5

“Meditationis est perscrutari occulta ; contemplationis est admirari
perspicua Admiratio generat quæstionem, quæstio investigationem,
investigatio inventionem.”—*Hugo de S. Victore.*

—“Cur spirent venti, cur terra dehiscat,
Cur mare turgescat, pelago cur tantus amaror,
Cur caput obscura Phœbus ferrugine condât,
Quid toties diros cogat flagrare cometas,
Quid pariat nubes, veniant cur fulmina coelo,
Quo micet igne Iris, superos quis conciat orbes
Tam vario motu.”

J. B. Pinelli ad Mazonium.



CONTENTS OF VOL. XXIII.

(SIXTH SERIES).

NUMBER CXXXIII.—JANUARY 1912.

	Page
Prof. L. N. G. Filon on the Investigation of Stresses in a Rectangular Bar by means of Polarized Light. (Plates I. & II.)	1
Dr. Herbert Stansfield and Mr. H. P. Walmsley on Changes in Diffraction Spectra produced by Aberration and the Aberration of an Echelon Grating. (Plates III. & IV.)...	25
Dr. J. R. Ashworth on the Magnetic Temperature Coefficients of the Ferro-magnetic Elements in Corresponding States .	36
Mr. Norman Campbell on Delta Rays	46
Dr. W. F. G. Swann : A Deduction of the Effects of Uniform Translatory Motion, from the Electrical Theory of Matter, without the Employment of a Transformation of the Electromagnetic Equations.....	64
Dr. W. F. G. Swann on the FitzGerald Lorentz Contraction, and an Examination of the Method of Determining the Motions of Electrons, when considered simply as Singularities, moving so as to satisfy the Electromagnetic Scheme .	86
Miss Ellen O'Connor on the Spectrum of the Magnesium High-frequency Arc. (Plate V.)	94
Mr. D. Tyrer on the Law of Molecular Attraction	101
Mr. E. W. B. Gill on the Variation with Distance of the Ionization produced by Röntgen Rays	114
Mr. Clinton J. Davisson on the Positive Thermions from the Salts of the Alkaline Earths	121
Mr. Clinton J. Davisson on the Rôle Played by Gases in the Emission of Positive Thermions from Salts	139
Prof. E. F. Burton and Mr. W. B. Wiegand on the Effect of Electricity on Streams of Water Drops. (Plate VI.)....	148
Prof. M. S. Smoluchowski on Opalescence of Gases in the Critical State	165
Mr. J. C. Pomeroy on the Charges on Thermions produced in Air and Hydrogen at Atmospheric Pressure.....	173
Mr. Horace H. Poole on the Rate of Evolution of Heat by Orange	183
Dr. J. N. Pring and Mr. A. Parker on the Ionization produced by Carbon at High Temperatures	192

NUMBER CXXXIV.—FEBRUARY.

	Page
Prof. J. Joly on the Radioactivity of the Rocks of the St. Gothard Tunnel	201
Mr. L. Vegard on the Properties of the Rays producing Aurora Borealis	211
Mr. Louis Vessot King on the Cosine Law of Radiation....	237
Mr. Louis Vessot King on Absorption Problems in Radioactivity. (Plate VII.)	242
Mr. J. H. T. Roberts on a Method of Investigating the Transpiration of Gases through Tubes	250
Dr. J. Robinson on Photo-Electric Fatigue	255
Prof. O. W. Richardson on the Electron Theory of Contact Electromotive Force and Thermoelectricity	263
Mr. Arnold L. Fletcher on the Radium Content of Secondary Rocks.....	279
Drs. F. Fajans and W. Makower on the Growth of Radium C from Radium B	292
Mr. H. G. J. Moseley and Dr. W. Makower on γ Radiation from Radium B	302
Prof. R. W. Wood on Diffraction Gratings with Controlled Groove Form and Abnormal Distribution of Intensity....	310
Prof. C. G. Barkla and Mr. L. Simons on Ionization in Gaseous Mixtures by Röntgen Radiation	317
Intelligence and Miscellaneous Articles:—	
Note to Paper in the December number, by Dr. J. W. Nicholson	333
On Methods of Harmonic Analysis, by Prof. T. R. Lyle and Prof. S. P. Thompson	334
On relations between Atomic Volumes and Spectra, by Prof. Dr. N. Reinganum.....	336

NUMBER CXXXV.—MARCH.

Prof. Percival Lowell on the Asteroids	337
Dr. Gwilym Owen and Mr. J. H. T. Roberts on the Effect of Clouds on Ionization	352
Messrs. J. H. T. Roberts and E. Meigh on the Instability of Gaseous Jets	368
Prof. Richard C. Tolman: Non-Newtonian Mechanics, The Mass of a Moving Body	375
Prof. A. Anderson: Theory of the Behaviour of the Quadrant Electrometer	380
Dr. C. V. Burton on the Micro-Azimometer: an Instrument for measuring small Angular Displacements	385
Dr. Norman Campbell on Ionization by Collision	400
Messrs. Karl Scheel and Wilhelm Heuse: Concerning the Thermal Expansion of Mercury, Remarks on a Paper by Callendar and Moss	412

	Page
Mr. Allan Ferguson on Photographic Measurements of Pendent Drops. (Plate VIII.)	417
Lord Rayleigh on Departures from Fresnel's Laws of Reflexion	431
Dr. H. Geiger and Mr. J. M. Nuttall on the Ranges of the α Particles from Uranium	439
Notices respecting New Books:—	
C. V. Durell's A Course of Plane Geometry for Advanced Students	445
Dr. W. P. Milne's Homogeneous Coordinates for use in Colleges and Schools	446
Prof. J. A. Fleming's The Propagation of Electric Currents in Telephone and Telegraph Conductors	446
Bulletin of the Bureau of Standards	447

NUMBER CXXXVI.—APRIL.

Sir J. J. Thomson on Ionization by Moving Electrified Particles	449
Prof. A. W. Porter on the Viscosity of Liquids	458
Dr. Norman Campbell on Ionization by Alpha Rays	462
Mr. S. A. Shorter on the Application of the Theory of Chemical Potential to the Thermodynamical Theory of Solutions.—Part II. The Effect of Pressure on Vapour-Pressure, etc.	483
Prof. Edward V. Huntington: A New Approach to the Theory of Relativity	494
Mr. S. B. McLaren on the Emission and Absorption of Radiation in any Material System and Complete Radiation	513
Dr. J. Robinson on the Photoelectric Properties of Thin Metal Films	542
Dr. S. R. Milner on the Virial of a Mixture of Ions	551
Mr. Karl T. Compton on the Influence of the Contact Difference of Potential between the Plates emitting and receiving Electrons liberated by Ultra-violet Light on the Measurement of the Velocities of these Electrons. (Plate IX.)	579
Prof. O. W. Richardson on some Applications of the Electron Theory of Matter	594
Dr. Georg von Hevesy on the Electrochemistry of Radio-active Bodies	628
Mr. Nevil Maskelyne on the Trisection of an Angle	646
Prof. W. H. Bragg on the Direct or Indirect Nature of the Ionization by X-rays	647
Mr. E. Buckingham on the Time-Scale	651
Mr. N. Eumorfopoulos on the Expansion of Mercury and of Quartz	653
Mr. R. D. Kleeman on the Law of Molecular Attraction	656
Mr. H. Davies on a Relation between Coefficients of Expansion of Liquids and their Critical Temperatures	657

	Page
Prof. H. A. Wilson on the Theory of Spectral Series	660
Mr. C. G. Darwin on the Effects of the Diurnal Rotation on the Upper Atmosphere	664
Dr. Norman Campbell on the Electrical Resistance of Xylol- Alcohol Mixtures	668
Dr. T. S. Taylor: A Determination of the Number of Ions produced by an Alpha Particle from Polonium	670
Prof. J. S. Townsend: The Charges on Ions	677
Prof. H. L. Callendar on the Absolute Expansion of Mercury. Reply to Criticisms by Scheel and Heuse	679
Dr. A. S. Eve and Mr. F. H. Day on the Absorption of Röntgen Rays in Air	683
Dr. Norman Campbell: Non-Newtonian Mechanics	688

NUMBER CXXXVII.—MAY.

Prof. R. W. Wood on Selective Reflexion, Scattering and Absorption by Resonating Gas Molecules. (Plates X.-XII.)	689
Prof. E. M. Wellisch and Prof. H. L. Bronson on the Distri- bution of the Active Deposit of Radium in an Electric Field	714
Mr. Harry C. Jones on Absorption Spectra and the Solvate Theory of Solution	730
Mr. Robert G. Lunnon on the Unilateral Conductivity of Sulphated Accumulator Plates	742
Prof. Henry A. Erikson on the Recombination of Ions in Carbon Dioxide and Hydrogen at Different Temperatures ..	747
Prof. A. Anderson and Mr. H. N. Morrison on Electric Cur- rents in Air at Atmospheric Pressure, with Remarks on Induced Contact Electromotive Forces	750
Prof. J. P. Kuenen on the Deduction of Thermodynamical Relations	752
Dr. E. B. Ludlam on the Action of Ultra-Violet Light on Chlorine	757
Mr. J. H. C. Searle on the Problem of the Weir	772
Dr. L. Silberstein on the Quaternionic Form of Relativity ..	790
Mr. Andrew Stephenson on the Propagation of Periodic Æther Disturbance	809
Mr. V. E. Pound on the Secondary Rays excited in the Alpha Rays from Polonium	813
Messrs. E. W. B. Gill and F. B. Pidduck on Ionization by Collision in Helium	837
Dr. Carl Ramsauer: Remarks on the Production of Con- densation Nuclei in Air and in Vapours by Intense Cooling and by Ultra-Violet Light	849
Prof. W. A. Douglas Rudge: A Note on the Electrification of the Atmosphere and Surface of the Earth	852
Prof. J. S. Townsend: Theory of Ionization by Collision ..	856

	Page
Miss Hilda P. Hudson on the Trisection of an Angle	860
Mr. T. J. I'a. Bromwich on the Trisection of an Angle	860
Mr. J. R. Cotter on the Trisection of an Angle	861
Notices respecting New Books :—	
Dr. A. E. H. Love's Some Problems of Geodynamics ..	862
Sir George Howard Darwin's The Tides and Kindred Phenomena of the Solar System	862
Dr. Andrew Gray and Dr. J. G. Gray's Treatise on Dynamics, with Examples and Exercises	863
Dr. Edwin H. Barton's Analytical Mechanics, com- prising the Kinetics and Statics of Solids and Fluids .	863
Publications of the U.S. Coast and Geodetic Survey ..	864

NUMBER CXXXVIII.—JUNE.

Dr. E. N. da C. Andrade on the Nature and Velocity of Migration of the Carriers of Electricity in Flames con- taining Metallic Vapours	865
Prof. E. H. Barton and Mr. W. B. Kilby on Simultaneous Vibration Curves for Strings and Air of Violin. (Plates XIII.—XV.)	885
Mr. Thomas H. Blakesley on a Kinematic Method of finding the Roots which are less than Unity of a Rational Integral Equation of any Degree: followed by a more general Method of finding the Roots of any Value	892
Mr. C. G. Darwin: A Theory of the Absorption and Scat- tering of the α Rays	901
Mr. E. Buckingham on the Deduction of Wien's Displace- ment Law	920
Mr. J. H. T. Roberts on Transverse Vibration of a String Maintained by Forces of Double Frequency	931
Mr. E. H. Kennard on Unipolar Induction	937
Prof. C. Barus on the Rectification of the Spectrum in Re- lation to the Shift of Ellipses in Displacement Inter- ferometry	942
Mr. W. Sukhodski on Mr. McC. Lewis's Papers on the In- ternal Pressure of a Liquid	955
Mr. J. Kendall on the Solubility of Calcium Carbonate in Water	958
Mr. A. I. Steven on the Composition of two Simple Harmonic Motions exhibited by a Stretched String. (Plate XVI.)..	977
Prof. H. A. Wilson on the Relation between the Ranges of α Particles and the Periods of Transformation of Radio- active Bodies	981
Mr. N. Bohr: Note on the Electron Theory of Thermoelectric Phenomena	984
Dr. Norman R. Campbell on the Theory of Ionization by Collision	986

	Page
Prof. C. G. Barkla and Mr. V. Collier on the Absorption of X-Rays and Fluorescent X-Ray Spectra	987
Prof. H. L. Callendar on Anisotropic Expansion of a Drawn Tube of Vitreous Silica	998
Notices respecting New Books:—	
Dr. G. W. C. Kaye and Prof. T. H. Laby's Physical and Chemical Constants and some Mathematical Functions	1000
Index	1002

P L A T E S.

- I. & II. Illustrative of Prof. L. N. G. Filon's Paper on the Investigation of Stresses in a Rectangular Bar by means of Polarized Light.
- III. & IV. Illustrative of Dr. H. Stansfield and Mr. H. P. Walmsley's Paper on Changes in Diffraction Spectra produced by Aberration and the Aberration of an Echelon Grating.
- V. Illustrative of Miss E. O'Connor's Paper on the Spectrum of the Magnesium High-frequency Arc.
- VI. Illustrative of Prof. E. F. Burton and Mr. W. B. Wiegand's Paper on the Effect of Electricity on Streams of Water Drops.
- VII. Illustrative of Mr. L. V. King's Paper on Absorption Problems in Radioactivity.
- VIII. Illustrative of Mr. Allan Ferguson's Paper on Photographic Measurements of Pendent Drops.
- IX. Illustrative of Mr. Karl T. Compton's Paper on the Influence of the Contact Difference of Potential between the Plates emitting and receiving Electrons liberated by Ultra-violet Light on the Measurement of the Velocities of these Electrons.
- X.-XII. Illustrative of Prof. R. W. Wood's Paper on Selective Reflexion, Scattering and Absorption by Resonating Gas Molecules.
- XIII.-XV. Illustrative of Prof. E. H. Barton and Mr. W. B. Kilby's Paper on Simultaneous Vibration Curves for Strings and Air of Violin.
- XVI. Illustrative of Mr. A. I. Steven's Paper on the Composition of Two Simple Harmonic Motions exhibited by a Stretched String.

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

JANUARY 1912.

I. *The Investigation of Stresses in a Rectangular Bar by means of Polarized Light.* By L. N. G. FILON, M.A., D.Sc., F.R.S., Assistant Professor of Mathematics at University College, London*.

[Plates I. & II.]

§ 1. *Introduction.*

THE question of the distribution of stress across the section of an elastic solid of rectangular shape has recently been receiving some attention, both theoretically and experimentally, chiefly in connexion with the problem of stresses in dams†. The experiments to be described were undertaken some years ago with a view to verifying the results of de Saint-Venant relating to the parabolic distribution of shear in a long bar of rectangular cross-section at a distance from the points of loading. The method was further applied to check certain theoretical results obtained by the author‡ regarding the distribution of stress in such a bar immediately below a concentrated load.

The method used depends on the well-known property of glass, that under mechanical stress it becomes doubly refracting, and a plane wave of light traversing it is broken

* Communicated by Prof. F. T. Trouton, F.R.S.

† Pearson and Atcherley, Drapers Company Research Memoirs, 1906.
L. F. Richardson, "The Approximate Arithmetical Solution by Finite Differences of Physical Problems," Phil. Trans. A. vol. ccx. pp. 307-358.
E. N. da C. Andrade, R. S. Proc., A. vol. lxxxv. pp. 448-461.

‡ L. N. G. Filon, Phil. Trans. A. vol. cci. pp. 63-155.

up into two plane-polarized components. The planes of polarization of these components are in the directions of the two principal stresses in the plane of the wave-front, and the relative retardation of the two components is jointly proportional to the difference of these principal stresses and to the thickness of glass traversed*.

If, then, we consider a thin plate of glass, of thickness τ , strained in its own plane, so that at any point the principal stresses are R, T , the relative retardation on emergence of two rays which entered the glass in the same phase and traversed the plate normally is

$$C\tau(R-T),$$

C being the relative stress-optical coefficient of the glass for light of the particular wave-length used†.

If such a plate of glass be introduced between crossed nicols, and viewed by homogeneous light through these nicols, light will be restored in the field except at such points of the plate where (1) $C\tau(R-T)$ is an integral multiple of the wave-length, or (2) the principal axes of stress are along the axes of the nicols. These give rise to two dark loci or bands in the field.

If now the homogeneous light be replaced by white light, the dark band corresponding to condition (2) occupies the same position for every kind of light. It therefore still appears *black* in white light. On the other hand, owing to change both of C and of the wave-length the locus corresponding to condition (1) varies with the nature of the light used. It therefore appears in the field of view as a coloured line, corresponding to the quenching of a certain part of the spectrum. We have then bands of the same colour corresponding to equal values of $R-T$ and black bands corresponding to points where the principal axes of stress in the plate have a constant direction, namely, those of the axes of the nicol.

These two types of bands have been called by Maxwell‡ the isochromatic lines and the lines of equal inclination respectively; we may call the latter isoclinic lines for brevity. As the nicols are rotated the isochromatic lines remain fixed, but the isoclinic lines vary.

* Brewster, Phil. Trans. 1816, p. 156; Fresnel, *Œuvres*, tom. i. p. 713; F. E. Neumann, *Abh. d. k. Acad. der Wiss. zu Berlin*, 1841 (ii.); Clerk Maxwell, Trans. R. S. Edin. vol. xx. p. 117 (1883); Wertheim, *Ann. de Chim. et de Physique*, série 3, vol. xl.; Dr. John Kerr, Phil. Mag. 1888, vol. xxvi. No. 161.

† Filon, Phil. Trans. A. vol. ccvii. pp. 263-306.

‡ Collected Papers, vol. i. pp. 30-73, "On the Equilibrium of Elastic Solids."

Maxwell himself, in the paper referred to, indicated the value of these lines for the purpose of experimentally determining the stress system inside an elastic solid, and gave several examples. Later, Professor Carus Wilson (Phil. Mag. ser. 5, Dec. 1891) applied the method to the investigation of the stresses in a beam bent by a central load, but restricted himself almost exclusively to the study of the stresses in the mid-section of the beam. He has, however, given a drawing of the isoclinic lines and deduced from them by Maxwell's method the lines of principal stress, but has not discussed them further.

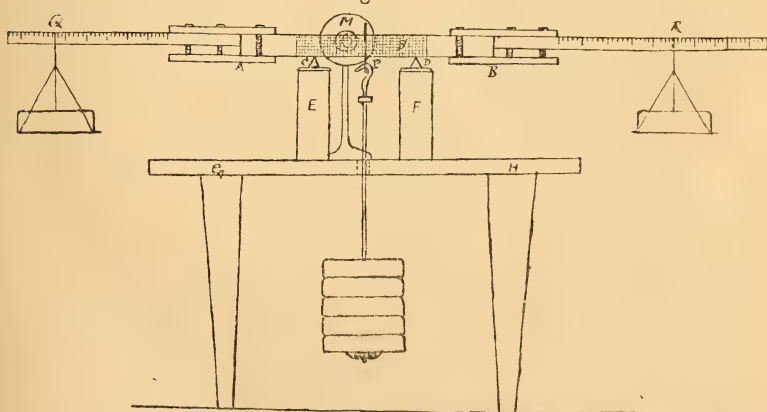
Quite recently Professor E. G. Coker, in a paper on the distribution of stress in plates of variable section, read before the Institution of Naval Architects, April 7, 1911, has applied the method to the study of problems connected with the effects of rivet holes; he has made use exclusively of the isochromatic lines.

The experiments of which the present paper gives an account were carried out in the Engineering Laboratory, Cambridge, in 1901, with the object of extending the results of Carus Wilson. Owing to various circumstances and pressure of other work, they have remained hitherto unpublished. Nevertheless the author believes that the same ground has not been covered since.

§ 2. *Description of Apparatus.*

Plate I. shows a photograph of the actual apparatus used, of which figs. 1 and 2 give a diagrammatic representation in plan and elevation.

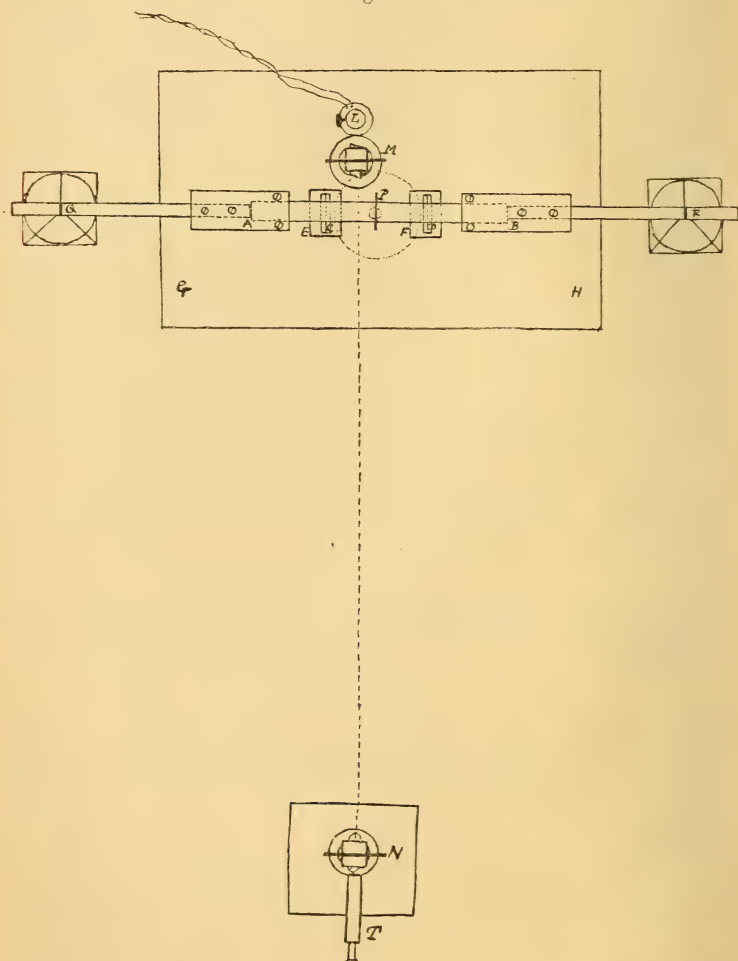
Fig. 1.



The glass bar AB, of rectangular section, rested on two knife-edges C, D, supported by two wooden blocks E, F,
B 2

which were screwed into a table GH. A central load was applied by placing weights upon a hanger P suspended from a knife-edge which rested on the upper surface of the bar.

Fig. 2.



In addition, a flexural couple, free from shear, could be applied to the bar by suspending weights symmetrically from light wooden arms AQ, BR, which were clamped to the extremities of the bar as shown in fig. 1, and projected several feet beyond the supporting knife-edges. An arrangement of levers and wires (shown in Plate I.) allowed such a couple to be applied in either sense.

The optical arrangements consisted in a source of light L (a portable electric lamp with a ground-glass globe was used), a polarizing nicol M, which was placed close behind the glass bar, and an analysing nicol N, which was placed on a small stand some distance away, and into which looked a telescope T. The latter was focussed upon a network S of squares of 5 mm. side, which was engraved upon a glass plate and placed in contact with one of the vertical side faces of the bar.

The method of observing was as follows:—the nicols M and N had their axes crossed and inclined to the vertical at the required angle. A sufficient load was then applied, and the corresponding isoclinic line traced by observing the position of the black band with regard to the squares of the network S and transferring it to squared paper.

The band had always a certain breadth, but, except on a few occasions, it was never so inconveniently broad as to prevent its centre from being located with fair accuracy.

In this way, by varying the inclination of the nicols to the vertical, charts of the isoclinic lines were obtained. From such charts the measurements were made of which the results are recorded.

§ 3. *Theoretical Results taken as the Basis of Comparison.*

If we consider the flexure of a rectangular bar of span $2a$, height $2b$, and breadth $2c$ in a vertical plane, the axis of x being the axis of the bar, the axis of y vertically upwards, and the axis of z perpendicular to the plane of bending, we notice first of all that in strictness the system of stresses P, S, Q acting in the planes parallel to xy (P being the normal tension across a face perpendicular to x , S the vertical shear across the same face, and Q the normal tension across a face perpendicular to y) is not independent of z , but varies as we move transversely across the bar.

If, however, this variation (at all events in so far as it affects the principal axes of stress) were at all serious, it would cause a variation in the axes of polarization of the transmitted light as it travelled through the beam. Such a variation would destroy all possibility of quenching the light between crossed nicols, and the mere fact of sharply defined black isoclinic lines being visible is evidence that the axes of polarization inside the glass remain fairly constant as we move across it transversely.

We may, therefore, assume without serious error that the stress system is approximately independent of z . In this

case the solution is well-known*. If M is the bending moment at any section *which is at a distance from the points of loading*, S_0 the total shear at that section, A the area of the cross-section, k the radius of gyration of this area about a horizontal through its centroid in its plane (the so-called "neutral axis"), we have

$$P = \frac{My}{Ak^2}, \quad S = \frac{3S_0}{2A} \left(1 - \frac{y^2}{b^2} \right), \quad Q = 0. \quad . \quad . \quad (1)$$

Now the inclinations (i) to the x -axis of the principal axes of stress at the point are given by the equation

$$\begin{aligned} \tan 2i &= \frac{2S}{P-Q} \\ &= \frac{3k^2 S_0}{M} \left(\frac{b^2 - y^2}{yb^2} \right) = \frac{S_0}{M} \frac{b^2 - y^2}{y}, \quad . \quad . \quad (2) \end{aligned}$$

since, the section being rectangular, $k^2 = b^2/3$.

It follows that if $y=0$ or $M=0$ (unless $S_0=0$ at the same time) $\tan 2i = \infty$ or $i = 45^\circ$, that is, when the nicols are at 45° to the vertical, the isoclinic line will be along the axis of the bar, and along the sections of zero bending moment.

If $i=0$, that is, when the nicols are horizontal and vertical, the isoclinic line should be along the top and bottom edges of the bar. To get the shape of the isoclinic lines for intermediate values of i we note that over any part of the bar which is free from loading

$$M = M_0 + S_0 x, \quad . \quad . \quad . \quad (3)$$

where M_0 is a constant.

If we measure x from a section of zero bending moment, this takes the form

$$M = S_0 x,$$

and we have for the isoclinic lines

$$xy \tan 2i + (y^2 - b^2) = 0. \quad . \quad . \quad . \quad (4)$$

These are a set of hyperbolas whose asymptotes are

$$y=0, \quad y + x \tan 2i = 0,$$

and all of which pass through the points

$$x=0, \quad y = \pm b.$$

* See Love, 'Theory of Elasticity.'

§ 4. *Comparison of Experimental Results with Theory.*

The general appearance of the bands, as soon as the distance from a point of loading exceeded the greatest dimension of the cross-section, corresponded closely with the theoretical results of the last article.

Quite recently I have been able, through the kindness of Prof. F. T. Trouton and Prof. A. W. Porter, to use the large nicols in the possession of the Physical Laboratory of University College, in order to photograph these bands, as shown by a specimen in a straining-frame; and although these are not the actual bands whose measurements form the subject of the present paper, they should be of identical shape.

The photographs of these bands are shown in Plate II., and by the side of each is placed a diagram of the corresponding theoretical hyperbola as given by (4). Any exact comparison is difficult, as the large thickness of the nicols used introduced an appreciable distortion in the images; this is clearly seen in the pictures from the curved appearance of the (really straight and parallel) edges of the glass. But the similarity is sufficiently close to afford, by itself, striking confirmation of the theoretical results.

In these pictures the inclination of the nicols increases by differences of 15° . One corresponds to an inclination of 49° , being the closest to 45° for which the two branches of the hyperbola were still clearly distinguishable, in spite of the dark region joining them.

In the Cambridge experiments the method of comparison adopted was as follows: a number of measurements were taken on the charts of the bands (mentioned at the end of § 2), giving for selected values of y and i a corresponding value of x .

Now if we write $K=3S_0/Ab^2$, we have from (1) and $M=S_0x$

$$2S=K(b^2-y^2), \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$P=K \cdot xy, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and also

$$\begin{aligned} \frac{2S}{K} &= \frac{P}{K} \tan 2i, \\ &= xy \tan 2i. \quad . \quad . \quad . \quad . \quad . \quad (7) \end{aligned}$$

$2S/K$ was then calculated by means of formula (7), the mean of a number of measurements on different charts being taken. This was compared with the values of b^2-y^2 . The results

are given in Table I. below. The bar of glass used was a bar of thick plate glass, made for me by the London and Manchester Plate Glass Company, St. Helens, and was practically free from imperfect annealing. The height, $2b$, was 3.60 cm.

TABLE I.

y .	$b^2 - y^2$.	$2S/K$.	$2S/K - (b^2 - y^2)$.	Percentage difference.
1.6	.68	.75	+.07	10
1.4	1.28	1.33	+.05	4
1.2	1.80	1.85	+.05	3
1.0	2.24	2.19	-.05	2
.8	2.60	2.68	+.08	3
.6	2.88	2.85	-.03	1
.4	3.08	2.83	-.25	8
-.4	3.08	2.88	-.20	7
-.6	2.88	2.84	-.04	1
-.8	2.60	2.49	-.11	4
-1.0	2.24	2.20	-.04	2
-1.2	1.80	1.79	-.01	1
-1.4	1.28	1.25	-.03	2
-1.6	.68	.59	-.11	16

Large errors occur for numerically small values of y , and no reliable measurements were found to give $2S/K$ for small values of y . This, however, is to be expected, since when y is small, $\tan 2i$ is very great and formula (7) is liable to large errors whenever a small absolute error is made in y . Large percentage errors also occur near the ends, but this is principally due to the smallness of the quantity on which the percentage is taken. A noticeable point is that the errors tend to be in a different sense on opposite sides of the neutral axis. Any small error in the determination of the neutral axis might easily account for this. Altogether, if the difficulty of measuring exactly bands of this nature be borne in mind, the results give, on the whole, very good confirmation of the accepted theory.

§ 5. *Experimental verification of the Bernoulli-Euler Theory of Flexure for a Beam under a pure couple.*

The apparatus described in § 2 allowed of the bar being strained under a pure couple. This was done by removing the central load altogether and suspending weights from the projecting ends.

It seemed of some interest to verify that in this case the assumptions of the Euler-Bernoulli theory are satisfied, viz.

in the notation of § 3, $S_0=0$, or

$$P = \frac{M_0 y}{A k^2}, \quad S=0, \quad Q=0. \quad . \quad . \quad . \quad . \quad (8)$$

For the purpose of this verification the isochromatic lines were used, as well as the isoclinic. For an isochromatic line, if $S=0$, $Q=0$, P should be constant. Hence, if equations (8) are correct, the isochromatic lines should be parallel to the horizontal edges of the bar. The isoclinic lines should reduce to a single dark band along the axis of the bar ($y=0$), except when $i=0$ or 90° , when the whole field should be dark.

The span of the beam between the supporting knife-edges being 30 cm. a sufficient couple was applied to make visible the coloured band of the first order, both above and below the neutral axis. The line where the red passes into the blue was very sharply defined and easily measured.

Measures were taken at the mid-section and at various distances from it. The results are given below.

TABLE II.

Distance from mid-section.	Distance of upper Isochromatic from upper edge.	Distance of black band from upper edge.	Distance of lower Isochromatic from upper edge.
- 14 cm.	·45 cm.	1·80 cm.	3·10 cm.
- 10 „	·45 „	1·80 „	3·10 „
- 5 „	·50 „	1·82 „	3·10 „
0 „	·50 „	1·82 „	3·10 „
+ 5 „	·47 „	1·78 „	3·10 „
+ 10 „	·45 „	1·77 „	3·10 „
+ 14 „	·45 „	1·77 „	3·10 „

In the above the two isochromatics are equally distant from the black band, and all three are horizontal, the divergences being within the error of observation. This shows that the stress difference is constant as we move parallel to the axis of the beam, and that the tension and pressure above and below are numerically equal at equal distances from the neutral axis.

The above observations were taken with the nicols inclined at 45° to the vertical. On rotating them the black band

remained stationary, but, as the inclination of the nicols to the horizontal diminished down to 15° and less, the breadth of this band increased until finally, when the axes of the nicols were horizontal and vertical, the whole field was uniformly dark. This proved that the axes of stress in the bar were everywhere horizontal and vertical, and consequently that the shear was zero everywhere.

These results were to be expected, since for this type of strain the equations of elasticity can be solved exactly; but it nevertheless appeared that an experimental verification was not without value, particularly as previous observers have generally used, in order to produce bending stresses in glass, a straining-frame equivalent to doubly supporting and centrally loading.

§ 6. *Bands under a Point of Concentrated Load. Theory.*

Coming now to the second part of the experiments, these were intended to verify certain approximate formulæ for the stresses in a bar in the immediate neighbourhood of a point of concentrated load.

In a paper "On an approximate solution for the bending of a beam of rectangular cross-section under any system of load," Phil. Trans. A. vol. cci. pp. 63-155, the author has shown (see pp. 92-94, formulæ (77)-(80)) that immediately below such a point, where a load W per unit breadth of the bar is applied, the stresses are given by

$$\left. \begin{aligned} P &= -\frac{W}{\pi r'} \cos \phi' + \frac{W y'}{\pi r'^2} \cos 2\phi' \\ &\quad - \frac{4W}{\pi b} \sum_{\nu=0}^{\infty} \left(\frac{r'}{b}\right)^{2\nu} H_{2\nu} \frac{\cos 2\nu\phi'}{(2\nu)!} - \frac{4W}{\pi b} \sum_{\nu=0}^{\infty} (-1)^\nu \left(\frac{r'}{b}\right)^\nu \frac{\cos \nu\phi'}{\nu!} H_\nu \\ &\quad + \frac{4W y'}{\pi b^2} \sum_{\nu=0}^{\infty} (-1)^\nu \left(\frac{r'}{b}\right)^\nu H_{\nu+1} \frac{\cos \nu\phi'}{\nu!} \\ Q &= -\frac{W}{\pi r'} \cos \phi' - \frac{W y'}{\pi r'^2} \cos 2\phi' \\ &\quad + \frac{4W}{\pi b} \sum_{\nu=0}^{\infty} \left(\frac{r'}{b}\right)^{2\nu+1} H_{2\nu+1} \frac{\cos 2\nu+1\phi'}{(2\nu+1)!} - \frac{4W y'}{\pi b^2} \sum_{\nu=0}^{\infty} (-1)^\nu \left(\frac{r'}{b}\right)^\nu H_{\nu+1} \frac{\cos \nu\phi'}{\nu!} \\ S &= \frac{W y'}{\pi r'^2} \sin 2\phi' \\ &\quad + \frac{4W}{\pi b} \sum_{\nu=1}^{\infty} \left(\frac{r'}{b}\right)^{2\nu} H_{2\nu} \frac{\sin 2\nu\phi'}{(2\nu)!} - \frac{4W y'}{\pi b^2} \sum_{\nu=1}^{\infty} (-1)^\nu \left(\frac{r'}{b}\right)^\nu H_{\nu+1} \frac{\sin \nu\phi'}{\nu!} \end{aligned} \right\}, \quad (9)$$

where x is measured horizontally from the point of concentrated

loading as before, y' is measured vertically downwards from the point of concentrated loading, $r' = \sqrt{x^2 + y'^2}$ is the distance from this point, $\phi' = \tan^{-1} \frac{x}{y}$ is the inclination of the radius vector from this point to the vertical, b has the same meaning as before, and the H 's are constants given by the following equations

$$\left. \begin{aligned} H_0 &= \int_0^\infty \left(\frac{u^2}{\sinh^2 2u - 4u^2} - \frac{3}{16u^2} \right) du \\ H_1 &= \int_0^\infty \left(\frac{u^3 + \frac{1}{2}u^2 + \frac{1}{8}u - \frac{1}{8}u e^{-4u}}{\sinh^2 2u - 4u^2} - \frac{3}{16u^2} \right) du \\ H_{2\nu} &= \int_0^\infty \frac{u^{2\nu+2}}{\sinh^2 2u - 4u^2} du \\ H_{2\nu+1} &= \int_0^\infty \left(\frac{u^{2\nu+3} + \frac{1}{2}u^{2\nu+2} + \frac{1}{8}u^{2\nu+1} - \frac{1}{8}u^{2\nu+1} e^{-4u}}{\sinh^2 2u - 4u^2} \right) du \end{aligned} \right\} (\nu > 0) \quad (10)$$

Also there is a constant couple on the bar adjusted so that there is no bending moment under the concentrated load, so that the above represent only the disturbing effect of this load in its immediate neighbourhood.

If in addition we superimpose the stress system due to any constant couple M_0 , we have the following additional terms in the stresses

$$P = -\frac{3M_0 y}{2b^3}, \quad Q = 0, \quad S = 0,$$

y being measured vertically upwards from the neutral axis. Hence

$$\begin{aligned} P - Q &= \frac{2Wy'}{\pi r'^2} \cos 2\phi' - \frac{8W}{\pi b} \sum_{\nu=0}^{\infty} \left(\frac{r'}{b} \right)^{2\nu} H_{2\nu} \frac{\cos 2\nu\phi'}{(2\nu)!} \\ &\quad + \frac{8Wy'}{\pi b^2} \sum_{\nu=0}^{\infty} (-1)^\nu \left(\frac{r'}{b} \right)^\nu H_{\nu+1} \frac{\cos \nu\phi'}{\nu!} - \frac{3M_0}{2b^3} (b - y'), \\ 2S &= \frac{2Wy'}{\pi r'^2} \sin 2\phi' + \frac{8W}{\pi b} \sum_{\nu=1}^{\infty} \left(\frac{r'}{b} \right)^{2\nu} H_{2\nu} \frac{\sin 2\nu\phi'}{(2\nu)!} \\ &\quad - \frac{8Wy'}{\pi b^2} \sum_{\nu=1}^{\infty} (-1)^\nu \left(\frac{r'}{b} \right)^\nu H_{\nu+1} \frac{\sin \nu\phi'}{\nu!}. \end{aligned}$$

Now if we retain only terms of order r' in these expansions,

we have the following approximate expressions

$$\left. \begin{aligned} P-Q &= \frac{2W y'}{\pi r'^2} \cos 2\phi' - \frac{8W}{\pi b} H_0 - \frac{3M_0}{2b^2} + \left[\frac{8WH_1}{\pi b^2} + \frac{3M_0}{2b^3} \right] y' \\ 2S &= \frac{2W y'}{\pi r'^2} \sin 2\phi'. \end{aligned} \right\}$$

Hence, i being the inclination of the nicols,

$$\tan 2i = \frac{(y' \sin 2\phi')/r'^2}{(y' \cos 2\phi')/r'^2 - \left(\frac{4H_0}{b} + \frac{3\pi M_0}{4Wb^2} \right) + \left(\frac{4H_1}{b^2} + \frac{3\pi M_0}{4Wb^3} \right) y'}. \quad (11)$$

Write for shortness

$$\frac{4H_1}{b^2} + \frac{3M_0\pi}{4Wb^3} = q,$$

$$\frac{4H_0}{b} + \frac{3M_0\pi}{4Wb^2} = qb'.$$

Then equation (11) may be written

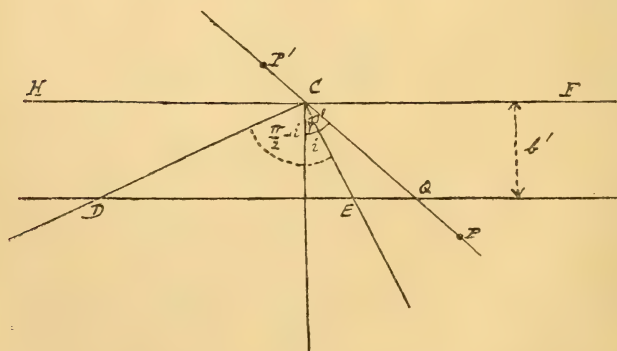
$$\frac{y'}{r'^2} \sin 2\phi' = \tan 2i \left(\frac{y' \cos 2\phi'}{r'^2} - qb' + qy' \right),$$

or

$$\frac{y'}{r'^2} \sin 2(\phi' - i) = (y' - b')q \sin 2i. \quad . \quad . \quad . \quad (12)$$

This may be expressed more concisely still in the following

Fig. 3.— $b' > 0$.



way. Let C (fig. 3) be the point of loading. Let DEQ be

a horizontal straight line drawn at a distance b' below it. Let the radius vector CP ($=r'$) cut DEQ at Q , and let $PQ=r_1'$, where the segment is to be taken with proper sign, the positive sense being from C to P . Then

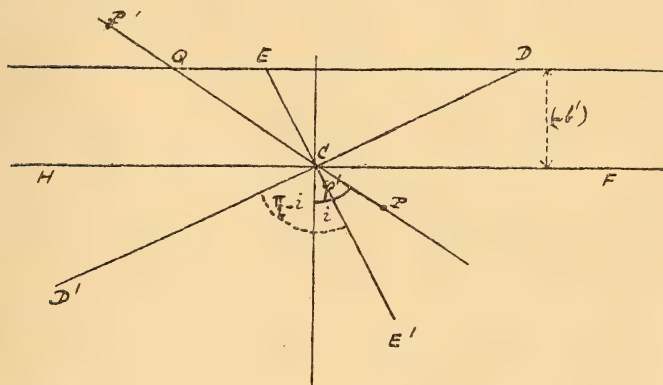
$$b'-y':y'=r_1':r',$$

and the equation to the isoclinic line takes the form

$$\sin 2(\phi'-i)=-r'r_1'q \sin 2i. \quad . \quad . \quad (13)$$

Now (Phil. Trans. A. vol. cci. p. 96) $H_0=-\cdot2417$, $H_1=-\cdot0598$, so that as M_0 increases from $-\infty$ to $+\infty$, q and qb' begin by being negative (*i. e.* $q<0$, $b'>0$): q changes sign first, and we have $q>0$, $b'<0$; then qb' changes sign and we have $q>0$, $b'>0$. In the first and third cases the figure is as in fig. 3, in the second case as in fig. 4.

Fig. 4.— $b'<0$.



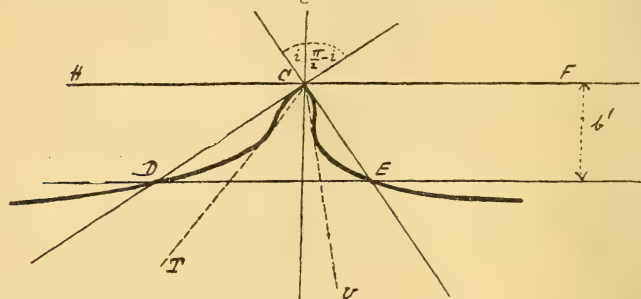
We have now to trace the form of the loci given by equation (13).

First we notice that since $r'+r_1'=b' \sec \phi'=CQ$, a second point P' of the locus is found by interchanging r' and r_1' , so that the two points P, P' on CQ divide the segment CQ symmetrically. Hence if $r'r_1'>0$ P, P' are between C and Q ; if $r'r_1'<0$ P, P' are outside CQ ; and this holds in all cases.

From equation (13) we have, since i is an acute angle, $\sin 2i>0$; therefore if $q>0$, P and P' are between C and Q if $\sin 2(\phi'-i)$ is negative, that is if CQ fall inside the quadrant DCE (fig. 3) bounded by $\phi'=i$, $\phi'=i-\frac{\pi}{2}$: outside this

quadrant P, P' are outside CQ; but if $q < 0$ P, P' are between C and Q outside DCE and inside CQ outside DCE.

Fig. 5.



The part of the plane which corresponds to the field of view is that below the horizontal through C; thus if $q > 0$, $b' > 0$ both P, P' are in the field inside DCE, but only one of them outside this angle. If $q > 0$, $b' < 0$, fig. 4 shows that no part of the curve is in the field within the angle DCE,

Fig. 6.

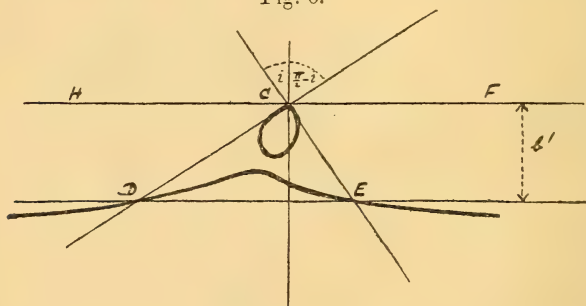
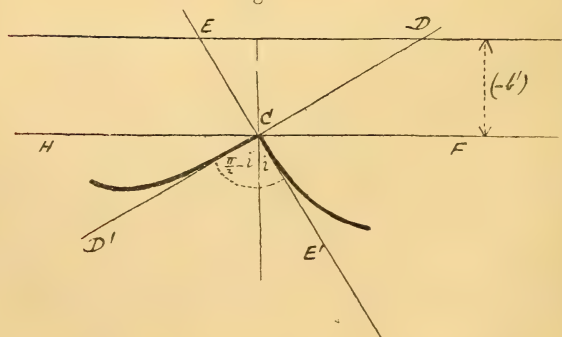


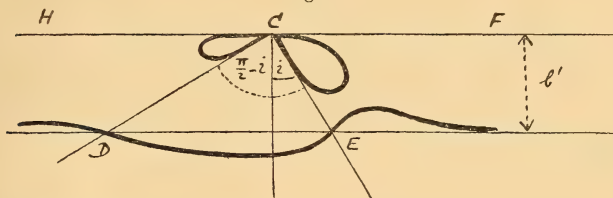
Fig. 7.



and one point P only outside DCE. Finally, if $q < 0$, $b' > 0$, one point P is in the field within DCE, and both P and P'

outside. The case $q < 0, b' < 0$ does not occur. The three cases just mentioned are illustrated by figs. 6, 7, and 8 respectively.

Fig. 8.



We have now to consider under what condition the points P, P' are real. Clearly the greatest possible algebraical value of $r'r_1'$ is $CQ^2/4 = (b'^2 \sec^2 \phi')/4$. If, then, P, P' are to be real, we must have

$$\frac{b'^2 \sec^2 \phi'}{4} > + \frac{\sin 2(i - \phi')}{q \sin 2i},$$

that is either

$$qb'^2 \sin 2i > 4 \cos^2 \phi' \sin 2(i - \phi') \quad (q > 0), \quad . \quad (14)$$

$$\text{or} \quad qb'^2 \sin 2i < 4 \cos^2 \phi' \sin 2(i - \phi') \quad (q < 0). \quad . \quad (15)$$

Let us write $u = 4 \cos^2 \phi' \sin (2i - 2\phi')$; then u is a maximum or minimum when

$$\frac{du}{d\phi'} = -8 \cos \phi' \cos (2i - 3\phi') = 0,$$

which gives the values

$$\phi' = \frac{\pi}{2} \quad (\text{maximum}), u = 0,$$

$$\phi' = \frac{2}{3}i + \frac{\pi}{6} \quad (\text{minimum}), u = -4 \sin^3 \left(\frac{\pi - 2i}{3} \right),$$

$$\phi' = \frac{2}{3}i - \frac{\pi}{6} \quad (\text{maximum}), u = 4 \sin^3 \left(\frac{\pi + 2i}{3} \right),$$

$$\phi' = \frac{2}{3}i - \frac{\pi}{2} \quad (\text{minimum}), u = -4 \sin^3 \frac{2i}{3},$$

$$\phi' = -\frac{\pi}{2} \quad (\text{maximum}), u = 0;$$

of these the second lies between $\phi' = i$ and $\phi' = \frac{\pi}{2}$, the third between $\phi' = i$ and $\phi' = i - \frac{\pi}{2}$, the fourth between $i - \frac{\pi}{2}$ and $-\frac{\pi}{2}$.

Also corresponding to the values $\phi' = i$, or $i - \frac{\pi}{2}$, $u = 0$.

Consider separately the cases where $q > 0$, $q < 0$ respectively. It will be convenient to discriminate briefly between the state of things in a sector in which every radius vector meets the curve in real points, and one in which a smaller sector is contained, in which there are no points of the curve. We shall speak of the first as a *loop*, of the second as a *fork*. These expressions are suggested by the forms shown in figs 5 and 6, but they are not to be regarded otherwise than as a convenient notation.

Case I., $q > 0$. For real values $qb'^2 \sin 2i > u$. Now in the sector ECF (fig. 3) u is zero at the boundaries of the sector and negative throughout. Thus real values exist and we have a *loop*. The reasoning on p. 14 then shows that every radius vector meets the curve in *one* real point in the field of view (see figs. 5, 6, and 7).

In the sector DCE, $u = 0$ at the boundaries and is positive throughout, having a maximum of $4 \sin^3 \left(\frac{\pi + 2i}{3} \right)$. Hence, according as $qb'^2 \sin 2i \gtrless 4 \sin^3 \frac{\pi + 2i}{3}$, we have a loop of the type shown in fig. 6 or a fork of the type shown in fig. 5.

We have, however, to show that qb'^2 is actually capable of taking up values that will ensure the occurrence of the two cases.

We have

$$\begin{aligned} qb'^2 &= \left(\frac{4H_0}{b} + \frac{3M_0\pi}{4Wb^2} \right)^2 / \left(\frac{4H_1}{b^2} + \frac{3M_0\pi}{4Wb^3} \right) \\ &= \left\{ \frac{4(H_0 - H_1)}{b} + bq \right\}^2 / q. \end{aligned}$$

For positive values of q (q is clearly capable of taking all possible values, by varying M_0) this has a minimum value zero when $q = 4(H_1 - H_0)/b^2$. For values of q smaller than this, $b' < 0$ and we have then seen that no part of the curve lies in the field of view.

We note also for future reference that for negative values of q there is an algebraic maximum when

$$q = -4(H_1 - H_0)/b^2,$$

giving

$$qb'^2 = 16(H_0 - H_1) = -2 \cdot 91. \quad \dots \quad (16)$$

Leaving such negative values of q out of consideration for the present, it appears that $qb'^2 \sin 2i$ can be made to range from 0 to $+\infty$. It can therefore be made either greater

or less than the positive quantity $4 \sin^3 \frac{\pi + 2i}{3}$. The critical value is given by

$$qb'^2 = 4 \sin^3 \left(\frac{\pi + 2i}{3} \right) / \sin 2i. \quad (17)$$

For this value the curve passes from the *loop* to the *fork* type, and we have a *node* or *cross* in the sector DCE.

In the sector DCH we have again u negative and a loop. The general character of the curve is the same as in the sector ECF.

Case II., $q < 0$. For real values $qb'^2 \sin 2i < u$. Now in the sector ECF we have a *fork* or *loop* according as

$$qb'^2 \sin 2i \gtrless -4 \sin^3 \left(\frac{\pi - 2i}{3} \right).$$

In the sector DCE we have always a loop, $qb'^2 \sin 2i$ being always negative, and therefore necessarily $< u$. This "loop" meets radii from C at one point, and is of the type shown in figs. 8, 9.

In the sector DCH we have a fork or loop according as

$$qb'^2 \sin 2i \gtrless -4 \sin^3 \frac{2i}{3}.$$

If we write $i' = \frac{\pi}{2} - i$, we have a fork or loop in ECF according as

$$qb'^2 \left(3 \sin \frac{2i'}{3} - 4 \sin^3 \frac{2i'}{3} \right) \gtrless -4 \sin^3 \frac{2i'}{3},$$

or, remembering that $0 < i < \frac{\pi}{2}$ and therefore $2i'/3$ and $2i/3$ are positive acute angles, according as

$$3qb'^2 \gtrless 4 \sin^2 \frac{2i'}{3} (qb'^2 - 1),$$

that is, q (and therefore $qb'^2 - 1$) being negative, according as

$$\sin^2 \frac{2i'}{3} \gtrless \frac{3qb'^2}{4(qb'^2 - 1)}. \quad (18)$$

Similarly we have a fork or loop in DCH according as

$$\sin^2 \frac{2i}{3} \gtrless \frac{3qb'^2}{4(qb'^2 - 1)}. \quad (19)$$

If i_0 be given by the equation

$$\sin^2 \frac{2i_0}{3} = \frac{3qb'^2}{4(qb'^2 - 1)}, \quad \dots \quad (20)$$

then we have a fork or loop in ECF according as

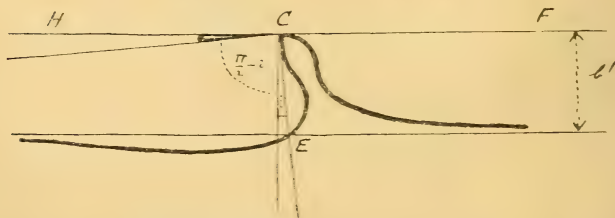
$$\frac{\pi}{2} - i \gtrless i_0,$$

and a fork or loop in DCH according as

$$i \gtrless i_0.$$

It appears from the last two inequalities (by addition) that if $\frac{\pi}{4} > i_0$ we can never have loops in both ECF and DCH simultaneously; if $\frac{\pi}{4} < i_0$ we can never have forks in these two sectors simultaneously. It appears also that, as qb'^2 increases negatively, i_0 steadily increases to 90° . Its lowest value corresponds to the numerically lowest negative value of qb'^2 , which we have seen to be -2.91 from equation (16). This gives for i_0 the value $72^\circ 30'$ nearly. It appears, therefore, that i_0 is always greater than this value. We have, therefore, for values of $i > i_0$ or $< \frac{\pi}{2} - i_0$ a fork in one sector and a loop in the other, as shown in fig. 9, and if

Fig. 9. $-i > i_0$ or $i \leq \pi/2 - i_0$.



i lies between i_0 and $\frac{\pi}{2} - i_0$ a loop in both sectors, as shown in fig. 8.

When q is small negatively, qb'^2 is a large negative quantity and i_0 is nearly 90° . We have therefore a loop in both sectors. As q increases negatively we find, if i exceeds $72^\circ 30'$, or falls below $17^\circ 30'$, that in one of the sectors the

loop passes over into a fork. As q increases further negatively, qb'^2 reaches its maximum and returns to the value $-\infty$. Thus after a time we have a second change, the fork passing over again into the loop. The two critical points correspond to the same value of qb'^2 , namely, that given by

$$qb'^2 = -4 \sin^2 \frac{2i}{3} / \sin 2i, \quad . \quad . \quad . \quad (21)$$

but to different values of q , there being two values of q for any given value of qb'^2 .

The reader should note that figs. 5-9 are merely diagrammatic, and are intended to give a rough sketch of the curves. They are not intended as accurate graphs.

§ 7. *Observation of the Isoclinic Lines near a point of concentrated load.*

The polarizer and analyser being crossed, their inclination to the horizontal and vertical was read. This gave the angle i . The ratio of M_0/W was then steadily varied by altering the forces acting on the projecting arms. Starting from a fairly large positive value M_0/W was diminished down to a fairly large negative value, i remaining constant all the time. This gave a range covering the various critical cases dealt with in the theoretical discussion of § 6.

The beam was examined for the values $0^\circ, 15^\circ, 30^\circ, 45^\circ, 60^\circ, 75^\circ, 90^\circ$ of i ; critical changes in the appearance of the black band were noted in each case.

The values $i=0$ and $i=90^\circ$ gave, as was to be expected, a vertical black band throughout, whatever the value of M_0/W .

For other values of i , starting from $M_0/W=7$ cm. (the height $2b$ of the bar being 3.60 cm.) the appearance of the black band first of all coincided with that shown in fig. 6. As M_0/W (and therefore qb'^2) decreases, we find that, as predicted from theory, the loop eventually passes into the fork. The values of M_0/W for which this occurred were noted for the various values of i . From these values of qb'^2 were obtained, and these were compared with the values of qb'^2 calculated from equation (17). The results of the comparison are shown in Table III. below.

TABLE III.

i .	M_0/W (observed) in centimetres.	qb'^2 (obs.).	qb'^2 (cal.).
15°	6.43	6.79	6.64
30°	4.44	4.21	4.41
45°	4.26	3.98	4.00
60°	4.83	4.71	4.41
75°	6.64	7.06	6.64

If we bear in mind that the exact moment when the fork passes into the loop is very difficult to determine experimentally, the field being very dark in the region where the change takes place, we may say that the experiments are in fair agreement with the theory within the limits of observation.

As M_0/W is still further diminished the fork of the band broadens out, and we observe the appearances shown in fig. 5. On continuing to decrease algebraically M_0/W , we eventually make $b' < 0$ and obtain the appearance shown in fig. 7. From this point, however, a difference occurs, according to the value of i taken. For $i = 30^\circ, 45^\circ, 60^\circ$, the two branches of the curve shown in fig. 7 gradually bend round until we get the double loop of fig. 8, after which no further critical change occurs. As M_0 increases negatively these loops gradually shrink, and soon present the appearance of two faint short brushes, which become practically invisible.

But for $i = 15^\circ$ or 75° (which gives $i > 72^\circ 30'$ or $< 17^\circ 30'$) the band first shows a fork in one sector as in fig. 9; when M_0/W passes a certain negative value, this fork passes into the double loop of fig. 8. This corresponds to the *second* critical point mentioned on p. 19. The existence of the first critical point, in which the loop passes into the fork, I have not been able to detect experimentally. The reason for this will be obvious if we look at the equations giving q and qb' . We see there that if q be very small, b' is very large (since qb' is not small with q). Now the node is always at a depth $b'/2$ below the point of loading. It follows that a node corresponding to a numerically small value of q will be outside the field of view, or, at all events, so far from the point of loading as to render our approximations invalid.

Turning to the actual numerical values obtained for the

critical point observed, they do not show very good agreement. The results are given in Table IV., the values in the column headed qb'^2 (cal.) being obtained from formula (21).

TABLE IV.

<i>i.</i>	M_0/W (obs.). in cm.	qb' (obs.).	qb'^2 (cal.).
15°	-2.04	-4.55	-3.60
75°	-2.40	-4.99	-3.60

The poor agreement may be due to two causes : (a) error in the determination of M_0 . This, although numerically small, had to be obtained as the difference of two numerically large couples, the determination of each of which was liable to error ; (b) the node was further from the point of concentrated load than in the case of Table III., and this, as pointed out above, may vitiate the approximations.

§ 8. Observations of the Points where the Isoclinic Lines cross the Vertical through the Load.

To further test the mathematical theory referred to, the points where the isoclinic lines crossed the vertical through the load were measured by means of the network of squares described in § 2, and compared with their positions as indicated by theory.

In the paper already referred to (Phil. Trans. A. vol. cci. pp. 63-155) the formulæ (86) given on p. 98 lead to the following expressions for $P-Q$, $2S$, when a couple M_0 is superadded.

$$\left. \begin{aligned} P-Q &= \frac{2W}{\pi b} \sum_0^{\infty} \left(\frac{r}{b}\right)^{\nu} \frac{\cos \nu \phi}{\nu!} G_{\nu+1} - \frac{2Wy}{\pi b^2} \sum_0^{\infty} \left(\frac{r}{b}\right)^{\nu} \frac{\cos \nu \phi}{\nu!} F_{\nu+1} - \frac{3M_0 y}{2b^3} \\ 2S &= \frac{2W}{\pi b} \sum_0^{\infty} \left(\frac{r}{b}\right)^{\nu} \frac{\sin \nu \phi}{\nu!} G_{\nu+1} - \frac{2Wy}{\pi b^2} \sum_0^{\infty} \left(\frac{r}{b}\right)^{\nu} \frac{\sin \nu \phi}{\nu!} F_{\nu+1} \end{aligned} \right\} . \quad (22)$$

The G 's and F 's are constants, having values given on p. 99 of the memoir referred to ; x and y are now measured horizontal and vertically upwards from the centre of the block of glass, $r = \sqrt{x^2 + y^2}$ and $\phi = \tan^{-1} x/y$.

Along the vertical through the load, x and therefore $\phi = 0$ and $r = y$. Thus $S = 0$ and the black band passes through those points for which $P - Q = 0$, whatever the value of i .

Such points are given approximately by the equation

$$\frac{2W}{\pi b} G_1 + \frac{2W}{\pi b^2} y (G_2 - F_1) - \frac{3M_0 y}{2b^3} = 0,$$

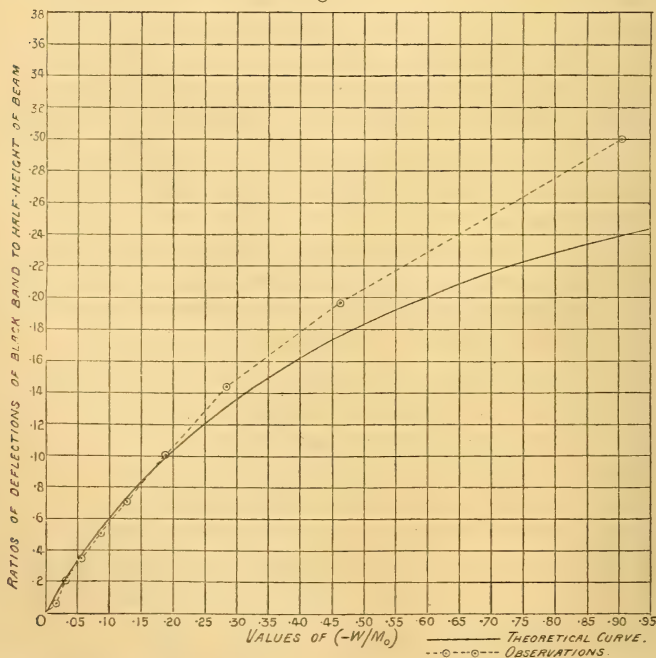
or putting in numerical values

$$\frac{y}{b} = - \frac{.3857 W/M_0}{W/M_0 - .5500} \quad \dots \quad (23)$$

The method adopted for testing this formula was to let the bending moment M_0 remain constant and to gradually increase W , observing the y of the point where the band crossed the central vertical. M_0 was negative throughout (*i. e.* it tended to produce bending in the opposite sense to W). y was therefore also negative.

The observations were repeated with three different values of i , namely, 30° , 45° , and 60° . It was verified that the point of crossing of the band was independent of i within the error of observation. The mean of the three readings was then adopted as being the true one.

Fig. 10.



The results are shown in fig. 10, the full curve showing the theoretical values calculated from (23), and the dotted

line the observations. The fit is strikingly close for small values of W , but the curves diverge as y increases. This is no more than we should expect, since the terms neglected in (22) then rise in importance. But where the formula is really valid the agreement is remarkable.

§ 9. *Observations of the Points where the Isoclinic Lines cross the Horizontal Axis of the Block.*

The same formulæ (22) allow us to bring yet another test to bear on the theory. To find where the band crosses the horizontal (or neutral) axis put in (22) $y=0$, $r=x$, $\phi=\pi/2$, and neglect terms of fourth and higher orders in x/b . We find

$$P - Q = \frac{2W}{\pi b} \left(G_1 - \frac{G_3}{2} \frac{x^2}{b^2} \right),$$

$$2S = \frac{2W}{\pi b} \left(G_2 \frac{x}{b} - \frac{G_4}{6} \frac{x^3}{b^3} \right).$$

Hence

$$\begin{aligned} \tan 2i &= \frac{G_2}{G_1} \frac{x}{b} \left(1 - \frac{G_4}{6G_2} \frac{x^2}{b^2} \right) / \left(1 - \frac{G_3}{2G_1} \frac{x^2}{b^2} \right) \\ &= \frac{G_2}{G_1} \frac{x}{b} \left[1 + \left(\frac{G_3}{2G_1} - \frac{G_4}{6G_2} \right) \frac{x^2}{b^2} \right], \end{aligned}$$

if x/b be small. Putting in numerical values from p. 99 of the memoir, we have

$$\tan 2i = 3.072 \frac{x}{b} + 5.115 \frac{x^3}{b^3}, \quad . \quad . \quad (24)$$

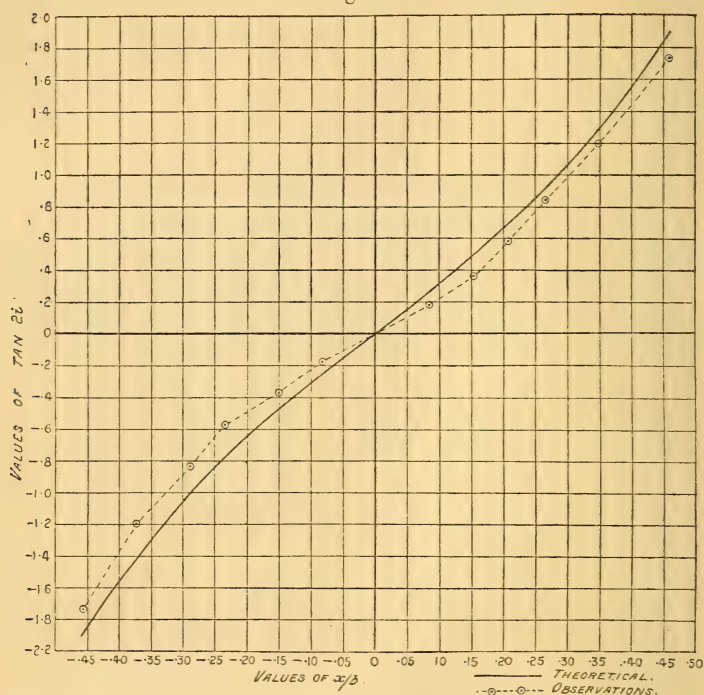
where i , x are to remain *small*.

When $i=0$ the band is vertical. Small positive values of i deflect it to the right; small negative values of i to the left.

These results were also verified experimentally, a set of simultaneous values of i and x/b being obtained. These are shown in fig. 11, $\tan 2i$ being plotted to x/b , and the full curve shows the graph of equation (24).

The agreement is here by no means so good as in fig. 10. Nevertheless the general nature of the two curves is the same. It should be noticed that a slight change in the vertical scale would give much closer agreement. This suggests an

Fig. 11.



error in the determination of the height $2b$ of the block, but there is no reason to doubt the accuracy of the latter measurement.

§ 10. Conclusion.

On the whole the investigation affords satisfactory confirmation of the results obtained from the mathematical theory of elasticity. It confirms the parabolic distribution of shear across a bar of rectangular section which is usually assumed by engineers, so long as we are at a reasonable distance from points of loading, and in the neighbourhood of points of loading it shows that the theory worked out by the author probably does give a fair representation of the actual distribution of stress.

It also shows the considerable value of the isoclinic lines in dealing with such "photoelastic" problems. The tendency of investigators has usually been to employ the isochromatic lines for this purpose. These, however, are in many ways inconvenient. To give accurate results, they involve the knowledge of the dependence of the stress-optical coefficient

on the wave-length and on the material. This requires a long preliminary investigation for every glass used. In the second place, if the field is to be adequately covered, a sufficient number of isochromatic lines must be brought into view. This involves the production of a very high stress, sometimes dangerously near the breaking-point. This must cause some plastic flow and permanent set, and so renders the method unsuitable for testing the results of the theory of elasticity.

On the other hand, the use of the isoclinic lines does away with these objections. The same results are obtained, whatever the photoelastic constants of the material, and a very moderate stress will show the effects. Indeed, to avoid confusion in the greater number of the experiments described above, the load was kept such that the isochromatic lines generally did not appear in the field of view.

In conclusion, I have to express my most hearty thanks to Sir Alfred Ewing, K.C.B., F.R.S., then Professor of Engineering in the University of Cambridge, for all his kind help and encouragement during the course of the work.

II. *Changes in Diffraction Spectra produced by Aberration and the Aberration of an Echelon Grating.* By HERBERT STANSFIELD, D.Sc., Assistant Lecturer and Demonstrator in the Physical Laboratories, Manchester University, and H. P. WALMSLEY, B.Sc., Graduate Scholar*.

[Plates III. & IV.]

IN the course of some previous experiments with an echelon grating, it was found that a bright line in the mercury green line spectrum was accompanied by a series of faint fine lines on the longer wave-length side†. Experiments made to test the origin of these faint lines proved that they were secondary maxima of the same wave-length as the bright line, for they moved farther away from the bright line when the number of apertures of the echelon was reduced.

Lord Rayleigh‡ has shown that a cubic aberration of a continuous wave-front increases the first secondary maximum on one side of the image and decreases the one on the other side. We find that similar results hold for a diffraction

* Communicated by the Authors.

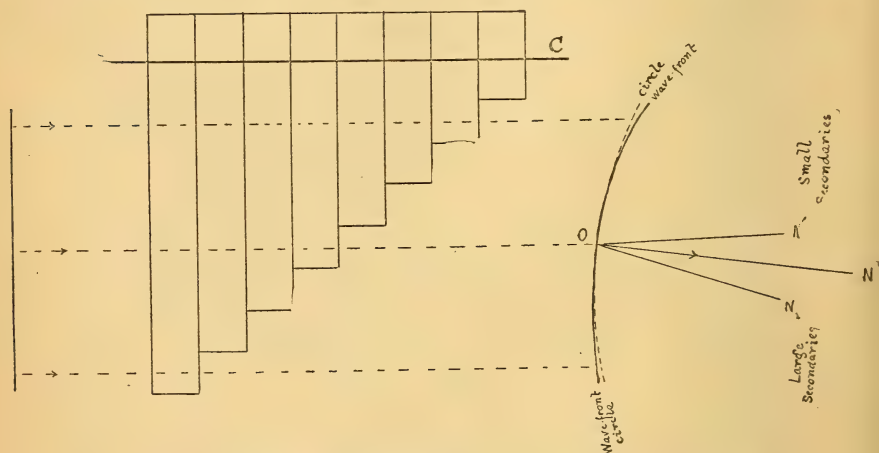
† Phil. Mag. vol. xviii. p. 371 (1909). Proceedings, Physical Soc. of London, vol. xxii. p. 822 (1910).

‡ Published Papers, vol. i. p. 430; Phil. Mag. vol. viii. p. 406 (1879).

grating, and that with a suitable amount of aberration four or five secondary maxima may be visible on one side of a bright line and none on the other.

In the case of the echelon grating we have employed the aberration is apparently produced by the clamping of the glass plates. We find that the echelon produces a slight curvature in wave-fronts or surfaces of equal phase passing through it. The light which issues from the small end of the echelon, and has passed through the parts of the plates which are most compressed, is slightly in advance of that which has passed through the plates farther from the clamping rods, as indicated diagrammatically in fig. 1, the position of the rods being indicated by the line CC.

Fig. 1.



If the curvature of the surface of equal phase were constant it would only produce a shortening of the focus of the observing telescope, which is a well-known feature*. The curvature increases, however, towards the side on which the plates are clamped, so that the dotted circle in fig. 1, coinciding with the middle of the surface, is in advance of the surface on the observer's left, and falls behind it on the right.

We find that the deviation of the surface from the circle can be nearly represented by a cubic aberration.

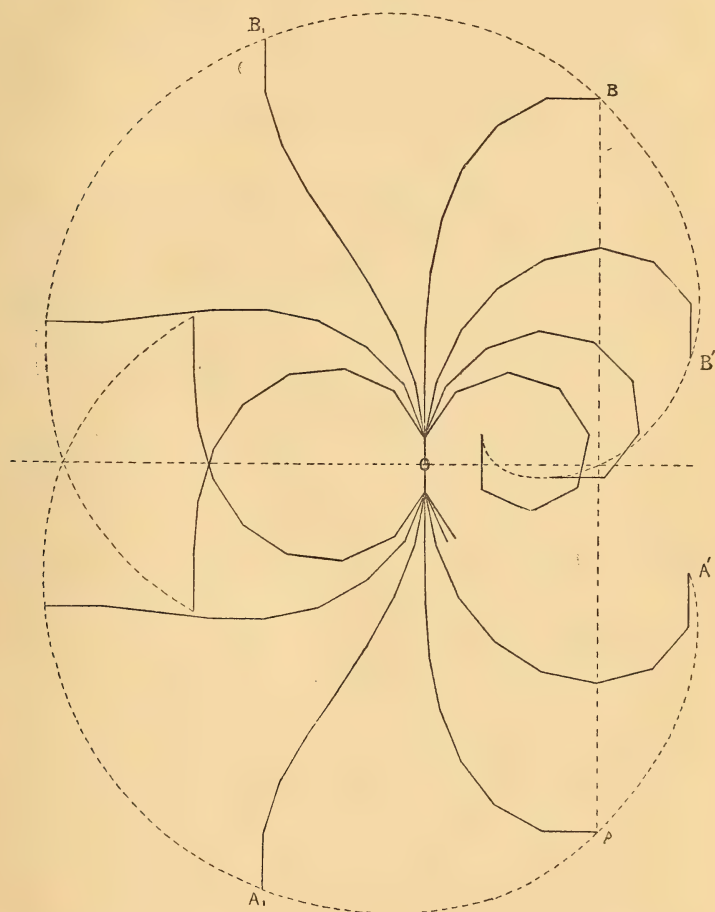
Calculation of the Effects of Cubic Aberration.

In order to find the effects which would be produced by cubic aberrations of the wave-front the distribution of light

* Phil. Mag. vol. xviii. p. 372 (1909).

has been calculated for a number of special cases. The method of calculation is represented geometrically in fig. 2,

Fig. 2.



where vector diagrams are drawn for a seventeen aperture diffraction grating with $\frac{1}{4}\lambda$ cubic aberration. ΔOB represents the phases of the disturbances transmitted in the direction of the normal to the wave-front at its centre, ON , fig. 1, the dotted line AB representing the resultant amplitude in this direction. Similarly $A'B'$ represents the amplitude in a direction ON' , fig. 1, such that the difference of phase between the light from the central and outside apertures is increased to 180° , and A_1B_1 the amplitude in a

direction ON_1 , making the same angle with the normal on the other side.

The vector diagrams are symmetrical about the horizontal axis, and the resultant amplitude vanishes for the cases where the two ends meet as they cross this centre line. Fig. 2 shows how much larger the first secondary maximum will be on the left side of this figure, where the aberration decreases the differences of phase, than on the right side, where the aberration increases the phase differences and helps to curl up the vector diagrams.

The values of the amplitudes for a nineteen aperture diffraction grating are represented in fig. 1, Pl. III., curves being drawn for the cases of zero, $\frac{1}{4}\lambda$, $\frac{1}{2}\lambda$, and $\frac{3}{4}\lambda$ aberrations. About eighty points were calculated for each curve by adding together the cosines of the phase-angles, four-figure values being employed. The horizontal scale represents direction, the normal to the centre of the wave-front being taken as origin, and the length of the diagram being the angular interval between the principal maxima.

The corresponding intensity curves are represented in fig. 2, Pl. III. These curves indicate the changes that would be produced in the appearance of the diffraction spectrum of a bright monochromatic source by varying degrees of aberration. Commencing with zero aberration, a few faint secondary maxima would be seen arranged symmetrically about the principal maximum. The curve drawn for $\frac{1}{4}\lambda$ aberration shows that this degree is sufficient to greatly increase the brightness of the secondaries on one side of the line, and to practically wipe out those on the other. With $\frac{1}{2}\lambda$ aberration the secondaries on the right are still further increased, and the principal maximum is reduced to $\cdot 74$ of its original brightness. The $\frac{3}{4}\lambda$ curve shows these changes carried still further, the bright line having now only about twice the intensity of the brightest secondary. The bright line also shows a considerable extension on the left, which would make it appear less sharp'y defined on that side than on the right, where it adjoins a bright secondary. It will be seen that in this case five secondaries on the right are brighter than the brightest of those on the left.

In calculating these curves no account has been taken of the variation with direction of the intensity of the light from the individual apertures of the grating. The form of the factor required to correct for this variation in the case of an ideal echelon, that is when the width of the aperture is equal to the grating interval, is represented by the dotted curve at the top of fig. 2, Pl. III.

In the case of a wire grating, referred to later on p. 33, the maximum of the dotted curve always coincides with the central principal maximum, but in the echelon case the relative position of the curves is not fixed, and any desired part of the spectrum may be moved into the position where the single aperture curve has its maximum, by a slight rotation of the echelon.

Position of the Secondary Maxima in the absence of Aberration.

If in plotting zero aberration amplitude curves the horizontal scale of direction is $N\theta$, where N is the number of apertures in the grating and θ half the phase difference between successive vectors for the given direction, then whatever the number of apertures in the gratings the curves will all cut the horizontal axis at the same points.

On plotting the zero aberration curves $\sin N\theta/N \sin \theta$ for gratings of nineteen and thirty-three apertures in this way it was found that these curves coincided very closely with one another, and with the $\sin N\theta/N\theta$ curve drawn to represent the case of a continuous wave-front or a grating with an infinite number of apertures.

As the curves agree so closely, we may say that for diffraction gratings with nineteen or more apertures and free from aberration, the relative intensity of the first three or four secondary maximum on either side of principal maxima and their distances from the principal maxima, expressed in terms of the interval between consecutive points where the intensity vanishes, are practically independent of the number of apertures in the grating.

In fig. 3, Pl. III., the $\sin N\theta/N\theta$ curve has been drawn, and it was found impossible to draw the zero aberration curves for nineteen and thirty-three apertures because they so nearly coincided with it.

Changes in the Position of Primary and Secondary Maxima produced by Aberration.

An examination of the curves of fig. 1, Pl. III., leads to the following rough rules for the displacements of the maxima:—A cubic aberration of the wave-front leaving a diffraction grating displaces the secondaries farthest from a primary maximum by approximately the same fraction of a complete cycle of the amplitude curve that the aberration between the centre and the outside of the wave-front is of the wave-length, and shifts the primary maxima through rather more than half this distance in the same direction. The

displacement is towards the side on which the aberration decreases the phase differences in the vector diagrams, and increases the intensities of the secondary maxima. The secondary maxima near to a primary are shifted less than those farther away, secondary maxima adjoining a primary maximum on the side where the secondaries are strengthened being displaced little more than the primary they adjoin.

It follows from the first rule that the displacement of the distant secondary maxima relative to the primary maxima is about the same fraction, mentioned above, of the half-cycle of the curve; the half-cycle being the interval between consecutive points where the zero aberration amplitude curve cuts the horizontal axis.

The displacements produced by various degrees of aberration, in the secondaries whose importance is increased by the aberration, are given in Table I., the position of any secondary in the case of a continuous wave-front free from aberration being taken as its standard position in finding the displacement. The values have been obtained by reading the positions of the maxima of amplitude curves drawn through a number of calculated points, and the second figure is in some cases only approximately correct.

TABLE I.

Displacements of Brightened Secondary Maxima relative to the Primary Maximum.

Aberration...	1/4 λ .		1/2 λ .		3/4 λ .		Standard distances.
	33	19	33	19	33	19	
1	·00	·01	·04	·04	·09	·10	1·43
2	·12	·13	·22	·23	·32	·34	2·46
3	·16	·18	·32	·35	·46	·50	3·47
4	·18	·21	·38	·41	·54	·60	4·48
5	·19	·22	·41	·44	·60	·66	5·48
6	·20	·23	·42	·45	·65	·70	6·48
7	·21	·24	·43	·46	·67	·73	7·49
P	·33	·35	·63	·69	·93	·99	

The distance of a secondary from its primary may be found by adding the value given for the displacement to the standard distance given in the last column. The bottom line gives the absolute displacements of the primary maxima. All the values are given in terms of the interval between successive points of zero intensity in the absence of aberration.

The $\frac{1}{4}\lambda$ aberration curve drawn in fig. 3, Pl. III., is intended to show the relative displacement of the primary and secondary maxima. The total difference of phase between the centre and outside of the wave-front is taken as the horizontal coordinate, 90° for the $\frac{1}{4}\lambda$ aberration being subtracted from $N\theta$, the difference of phase corresponding to the direction in the absence of aberration. When the curves for various degrees of aberration are plotted in this way the distant secondaries are only slightly shifted by the aberration, their relative displacement being represented by the movement of the principal maximum to the left.

The values given by Lord Rayleigh* for a continuous wave-front with $\frac{1}{4}\lambda$ aberration are also plotted in fig. 3, Pl. III., for comparison with the curves for finite numbers of apertures.

When aberration is present the effect of the number of apertures on the position of the secondaries is increased. Table I. shows the effect of changing the number of apertures from nineteen to thirty-three.

The displacements of the secondary maxima, brightened by the aberration, away from the primary (given in Table I.) may be employed to determine the amount of aberration present in a diffraction spectrum if a photograph showing a few secondary maxima can be obtained. Fig. 3, Pl. IV., is reproduced from a photograph of the green mercury line $5461 \text{ \AA}$, taken with the 33 aperture echelon we have employed, which has been already described†. This photograph shows secondary maxima on the right of the spectrum lines, and six secondaries of the line 1 were measured in the open space between the lines 1 and 2. The distances of these secondaries from their primary were divided by $1/33$ of the interval between successive repetitions of the primary lines, and the amounts by which the values found exceeded the standard distances for these secondaries are given below, together with the $\frac{3}{4}\lambda$ displacements taken from Table I. for comparison.

Photograph...	·02	·25	·42	·52	·54	·58
$\frac{3}{4}\lambda$, 33	·09	·32	·46	·54	·60	·65

These numbers show that the aberration when the photograph was taken was a little less than three-quarters of the wave-length.

It is also interesting to notice that the upper part of this photograph, which was given a long exposure, shows signs

* Lord Rayleigh's Published Papers, vol. i. p. 430.

† Phil. Mag. [6] vol. xviii. p. 371 (1909).

of the unsymmetrical broadening of the primary lines away from the bright secondaries, which would be expected from the shape of the intensity curve for $\frac{3}{4}\lambda$ aberration already referred to on p. 28.

It may also be mentioned that if the aperture of the echelon is reduced from 33 to 14 steps—which would reduce the maximum cubic aberration from $\cdot75\lambda$ to $\cdot057\lambda$ —the first secondary maxima of the line 1 appear as faint lines of equal intensity on either side of it.

Scale of Intensity provided by the Secondary Maxima.

The intensities of the first seven secondaries on the side where they are brightened by the aberration are given, for the special cases we have plotted, in Table II. The corresponding values for the standard case are also given for comparison.

TABLE II.

Relative Intensities of Primary and Secondary Maxima for the first seven Secondaries on the brightened side.

Aberration...	$1/4\lambda$.		$1/2\lambda$.		$3/4\lambda$.		0.
Number of apertures ...	33	19	33	19	33	19	∞
P	1	1	1	1	1	1	1
1	$\cdot14$	$\cdot154$	$\cdot30$	$\cdot32$	$\cdot54$	$\cdot61$	$\cdot0472$
2	$\cdot042$	$\cdot045$	$\cdot10$	$\cdot12$	$\cdot24$	$\cdot28$	$\cdot0165$
3	$\cdot017$	$\cdot019$	$\cdot042$	$\cdot05$	$\cdot10$	$\cdot12$	$\cdot0083$
4	$\cdot009$	$\cdot011$	$\cdot020$	$\cdot02$	$\cdot048$	$\cdot06$	$\cdot0050$
5	$\cdot006$	$\cdot0069$	$\cdot011$	$\cdot014$	$\cdot028$	$\cdot03$	$\cdot0034$
6	$\cdot004$	$\cdot0050$	$\cdot007$	$\cdot009$	$\cdot016$	$\cdot02$	$\cdot0024$
7	$\cdot003$	$\cdot0040$	$\cdot005$	$\cdot006$	$\cdot010$	$\cdot01$	$\cdot0018$
P	$\cdot94$	$\cdot93$	$\cdot76$	$\cdot74$	$\cdot54$	$\cdot50$	1

The intensities of the secondaries are expressed in terms of the intensity of the primary to which they belong. The bottom line gives the relative intensities of the primaries.

When the aberration in an echelon spectrum is large, the series of secondary maxima which appear in the photographs provide a convenient scale of relative intensities which may possibly prove useful in comparing the intensities of spectrum lines. For example, referring again to the photograph of the green mercury line in Plate IV., the intensity of the

image of the line 8 in the original negative, or in one of the enlargements, might be matched against the intensity of one of the secondary maxima of the line 1. Knowing the relative intensity of the line 1 and its secondary, a rough comparison of the lines 1 and 8 could be made.

A direct Method of Testing for Aberration.

The presence of cubic aberration in the echelon spectrum has been confirmed by direct measurements of the shape of the wave-fronts as they leave the echelon. This was done by measuring the very small displacements of a spectrum line, in the focal plane of the telescope, when different parts of the aperture of the echelon were exposed. We could not reduce the aperture to less than one-third of the full width without sacrificing too much the definition of the line to be measured; so groups of eleven steps were uncovered. Keeping the number of apertures constant, the group was moved across from one side of the echelon to the other, while readings of the position of the line 1 in the green line spectrum were made with a micrometer eyepiece. The variations of these readings were plotted against the corresponding positions of the centre of the group and a curve drawn which gave a close approximation to the direction of the wave-front for the central two-thirds of the aperture of the echelon, so the shape of the wave-front in this region could be found by integrating. The chief difficulty of obtaining a satisfactory set of readings was that the temperature generally altered too much while they were being made.

The results we have obtained show the wave-front concave towards the observer, the curvature at the centre agreeing fairly well with the observed shortening of the focus, and also give clear evidence of a cubic aberration. The magnitude of the aberration appears to be about $\cdot 3\lambda$ at the limits of the central $2/3$ of the aperture, which would correspond to about one wave-length for the edges of the full aperture. Owing to the temperature difficulty we can only regard this result as confirming the existence of a cubic aberration.

Experiments on producing Aberration.

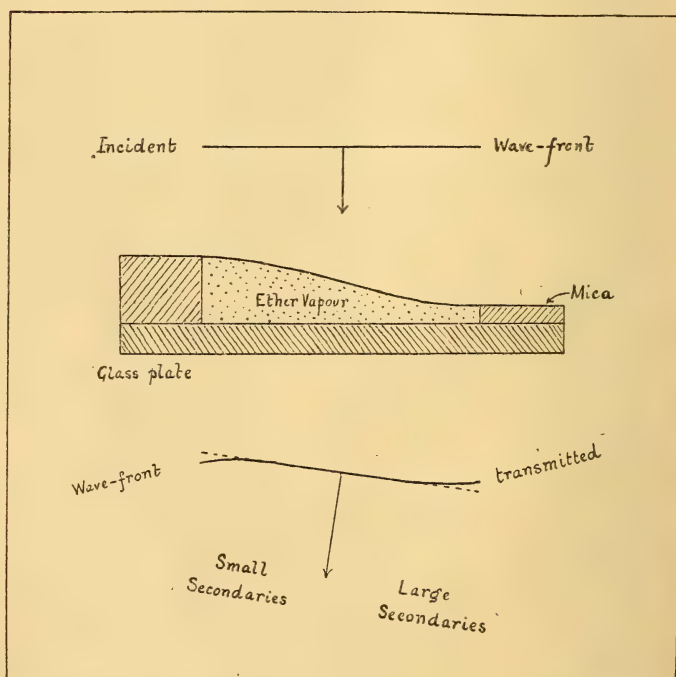
In order to commence with a very simple case, a diffraction grating was made with parallel wires $\cdot 2$ mm. diameter, spaced 1 mm. apart by means of two screws of millimetre pitch. No. 1, Pl. IV., is a photograph of the spectrum formed by this grating with green mercury light. Eight apertures were exposed when the photograph was taken, so that between

Phil. Mag. S. 6. Vol. 23. No. 133. Jan. 1912. D

two neighbouring primary maxima there are six secondaries, which all show clearly in the first order left and right in the original negative. As there is in this case no aberration, the secondaries are symmetrical on the two sides of the central primary maximum.

To produce aberration we made use of Lord Rayleigh's suggestion of employing the cubic curve associated with a bent plate*. A bent sheet of mica formed one side of a cell which was filled with ether vapour. In fig. 3 a section of

Fig. 3.



Section of Aberration Cell and Diagram of Changes produced in a Wave-front passing through it.

the cell is drawn together with a diagrammatic indication of the changes in direction and form produced in a wave-front passing through it.

* Rayleigh, Coll. Works, vol. iii. p. 59, note. Phil. Mag. vol. xv. p. 554 (1908).

When this cell was placed in front of the wire grating it produced little effect on the spectrum before the vapour was introduced, as both the glass plate and mica were sufficiently uniform in optical thickness; but when it was filled with ether vapour the secondaries on the observer's right in fig. 3 became much brighter than before, and those on the other side very faint.

We did not obtain a photograph showing the full effect owing to the difficulty of keeping the density of the vapour constant for a sufficient length of time; but No. 2, Pl. IV., taken under these conditions, shows the first secondary on the right much brighter than anything on the other side.

Summary.

1. Lord Rayleigh's investigation of the effects of cubic aberration has been extended to the first seven secondary maxima on either side of the primary, with special reference to the secondary maxima in diffraction spectra.

2. It has been found that a cubic aberration amounting to three-quarters of a wave-length at the edges of the aperture of the echelon we have employed is sufficient to explain why photographs taken with it show a series of secondary maxima on one side of a bright line and not on the other.

3. The degree of aberration present in an echelon spectrum may readily be determined by measuring the distances of the brightened secondaries from the primary to which they belong.

4. When the aberration in an echelon spectrum is relatively large the series of brightened secondary maxima provide a convenient scale of intensity which may be found useful in comparing the intensities of lines in the spectrum.

5. Photographs have been taken showing the effect of an aberration cell on the secondary diffraction maxima of a wire grating.

In conclusion, we wish to give our best thanks to Professor Rutherford and to Professor Schuster for placing the facilities of the Physical Laboratories at our disposal and for the interest they have taken in our work.

III. *The Magnetic Temperature Coefficients of the Ferromagnetic Elements in Corresponding States.* By J. R. ASHWORTH, D.Sc.*

1. Introduction, and initial statement of the final result.
2. Description of experimental work.
3. Results of experiments in tables and diagrams.
4. Comparison of results with similar experiments by other observers.
5. Reduction of results to corresponding states and conclusion therefrom.
6. Comparison with the temperature coefficient of density of a liquid.
7. Curie's law for paramagnetics.
8. Analogy between fluids and ferromagnetics.

1. **A**FTER a magnet has been repeatedly heated and cooled over a given range of temperature the magnetic intensity falls and rises regularly and in general without hysteresis as the temperature is raised and lowered. It has been shown that the magnitude of this effect of change of temperature on the magnetic intensity is largely controlled by the dimension ratio of the magnet, and that when this ratio is very large, so that the demagnetizing factor is negligible, the temperature coefficient is then a minimum, and under these conditions is *characteristic* of the material of the magnet †.

In the course of experiments on this subject, it was observed that the temperature coefficient of nickel was large, that of iron small, and that of cobalt still less, the values then obtained over a range of temperature of 90° , from 10° to 100° C., being about 6×10^{-4} for nickel, 2×10^{-4} for iron, and 1.5×10^{-4} for cobalt.

A preliminary calculation indicated that the characteristic coefficients were a function of the critical temperatures of these ferromagnetics, a result which demanded a more complete investigation. This has now been made, and the present paper is a record of experiments upon the variation of residual magnetic intensity of magnets made of nickel, iron, and cobalt of large dimension ratio, containing as little impurity as possible, when the temperature fluctuates between that of the atmosphere and the critical temperature.

The evidence now obtained supports the tentative conclusion mentioned above, and allows the general statement to be made that *the characteristic temperature coefficients of*

* Communicated by the Author.

† Ashworth, Roy. Soc. Proc. vol. lxii. p. 221 (1897); Phil. Trans. Roy Soc. vol. ciii., 1903.

magnetic intensity of the pure annealed ferromagnetic elements in corresponding states are inversely proportional to the absolute critical temperatures.

2. The experimental work leading to this result was made in two series. In the first wires of nickel and iron of large dimensions were employed. They were annealed, magnetized to saturation, heated to a little below the critical temperature, and then inserted in a glass tube containing olive oil, and in some of the later experiments in a brass trough containing sand. The heating was effected by a double row of many small Bunsen flames, and the magnetism of the wire was tested by placing it "end on" to a mirror magnetometer, the reflected beam of light being received on a scale two metres away. An electrical resistance thermometer which was laid side by side with the magnetized wire was used to measure the temperature. With this apparatus experiments were made up to 435°C . on a wire of nickel, two of soft iron, and a bundle of seven fine iron wires.

Difficulties, however, were experienced in procuring cobalt of the requisite dimensions, and the samples obtained contained too much impurity to yield trustworthy results. It was decided, therefore, to prepare cobalt electrolytically, and this led to the second series of experiments in which much smaller magnets were employed. These had the advantage that they could be heated uniformly with less probable error, but on account of their small mass, their magnetic moment was not large enough to give a deflexion of the magnetometer needle which could be read with accuracy.

This consideration necessitated the construction of a special magnetometer in which the single needle was replaced by a vertical astatic pair, 0.7 mm. apart and 13 cm. long, surrounded by a stout copper tube which served to damp the oscillations of the system. The orientation of the needles was read as before by a beam of reflected light on a scale two metres from the magnetometer.

This instrument was highly sensitive to any force acting on one pair of poles in the same horizontal plane, and was but little affected by extraneous disturbances so that it was very suitable for the purpose in hand, but it was not so convenient for the determination of absolute values.

Cobalt was now deposited electrolytically from a solution of the double sulphate of cobalt and ammonia on wires of copper and platinum 0.55 and 0.35 mm. in diameter respectively, and from 10 to 15 cm. in length. Each wire thus coated was

annealed, magnetized, and fixed inside a stout copper tube "end on" to the upper pair of poles of the astatic system. The temperature, which could be raised to 800°C. by a row of broad Bunsen burners, yielding a continuous sheet of flame, was observed by means of a thermo-junction of platinum and platinum-iridium, constructed by the Cambridge Scientific Instrument Co. The constant of the junction was verified and found correct. Thin wires of iron containing 0.4 per cent. of impurity, and of nickel with less than 2 per cent. of impurity, were also tested with this apparatus, and the results agreed closely with those of the first series.

The general course of an experiment was to heat and cool the magnet several times until a cyclic condition was reached, and then to take a careful set of simultaneous readings of magnetic intensity and temperature as the tube was slowly and continuously heated to the highest temperature required, and then allowed to cool. After this the magnets were re-magnetized and the experiment repeated for the sake of confirmation. The arrangements were such that the observations of temperature covered a range of 45 cm. for 800°C. and the readings of variation of magnetic intensity extended over 7.5 to 20.0 cm.

3. The results which have been arrived at are exhibited in Table I. and in fig. 1 (p. 40). In the first column of the table is given the temperature in centigrade degrees, and in the second column this temperature, converted into absolute degrees, is expressed as a fraction of the absolute critical temperature. In the third column is given the magnetic intensity calculated as a fraction of the intensity under the given conditions at absolute zero. The figures in the second and third columns have been carried to the third decimal place so that the second may be correctly assessed.

From the rate of change of intensity at ordinary temperatures the maximum intensity at absolute zero has been estimated, but there are experiments by P. Weiss and H. Kamerlingh Onnes* which show that the change of intensity from 0°C. to the temperature of liquid hydrogen under very strong forces is 5.5 per cent. for nickel and 2 per cent. for iron. I have adopted these values for nickel and iron, which are nearly the estimated values, and 1.5 per cent. for cobalt.

The critical temperature is taken to be that point at which the magnetic intensity is varying most rapidly with change of temperature. This I determined for nickel to be 388°C. , and for iron 785°C. , and I have adopted 1090°C. as the

* *Journal de Physique*, ser. 4, vol. ix. p. 555.

TABLE I.

Relation of Residual Magnetic Intensity to Temperature.

NICKEL.			IRON.			COBALT.		
Temp. C°.	θ/θ_1 .	I/I_0 .	Temp. C°.	θ/θ_1 .	I/I_0 .	Temp. C°.	θ/θ_1 .	I/I_0 .
21	·440	·945	17	·272	·981	14	·211	·985
50	·484	·931	40	·293	·977	115	·286	·984
76	·527	·917	90	·342	·969	209	·355	·975
107	·581	·900	138	·386	·960	300	·422	·954
135	·618	·884	188	·435	·949	390	·488	·933
165	·661	·861	237	·480	·936	472	·545	·910
193	·707	·837	287	·527	·921	560	·613	·877
223	·749	·801	337	·575	·902	645	·674	·839
251	·791	·761	386	·622	·877	747	·749	·786
280	·835	·714	435	·669	·842	1090	1·000	...
310	·882	·660	467	·700	·801			
323	·900	·630	530	·759	·793			
341	·929	·590	550	·776	·793			
352	·945	·554	593	·818	·763			
360	·956	·545	623	·845	·691			
365	·965	·509	650	·872	·654			
367	·967	·483	681	·901	·637			
388	1·000	(·355)	700	·920	·590			
			725	·943	·534			
			748	·965	·462			
			769	·984	·403			
			778	·992	·374			
			782	·996	·346			
			785	1·000	(·305)			

The dimensions of the wires were :

Nickel	1st series.	Length=63·5 cm.	Diameter=0·129 cm.
	2nd "	" =20·0 "	" =0·050 "
Iron	1st "	" =75·0 "	" =0·262 "
	2nd "	" =19·4 "	" =0·057 "
Cobalt	2nd "	" =about 10 cm.	" =about 0·1 cm.

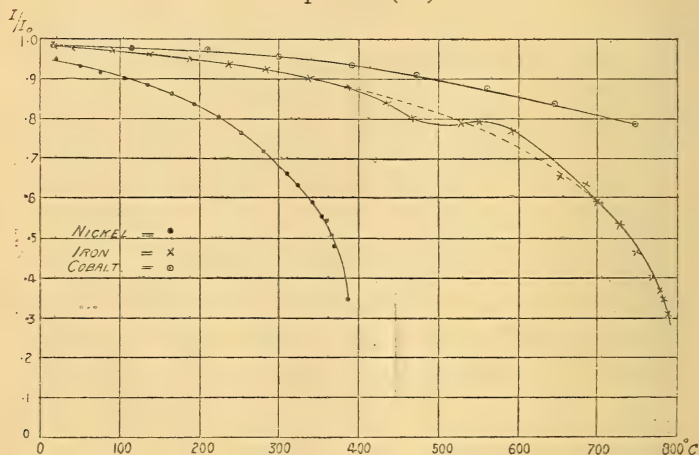
point of transformation of cobalt. If the magnets are not heated above the critical temperatures the magnetism, which falls at that point to about 30 per cent. of its initial value, remains cyclic and is entirely recovered on cooling.

The first diagram gives the variation of the fractional magnetic intensity (I/I_0) of each of the ferromagnetic metals compared with the temperature in centigrade degrees.

The curve for nickel is the mean of observations on two nickel wires, the individual observations agreeing very well with each other. Nickel behaves very regularly under increase of temperature, the curve declining smoothly and with increasing rapidity to about 35 per cent. of its original

value, when there is a sudden drop to about 5 or 6 per cent., after which the magnetism diminishes more slowly.

Fig. 1.—Relation of Fractional Magnetic Intensity (I/I_0) to Temperature ($^{\circ}\text{C}.$).



The curve for iron falls smoothly up to about $400^{\circ}\text{C}.$ when a more rapid fall begins followed by a halt or even rise of magnetic intensity between 500° and 600° , after which the diminution continues in a similar way to nickel, until at 30 per cent. of the original intensity the abrupt drop to a much lower value occurs. The irregularity at 420° to 620° embraces the region where there is an evolution of heat, discovered by Roberts-Austen *, which he says is not sudden but covers a range of 100° to 180° . It is no doubt associated with the point which has been designated ArO . Changes in electrical resistance have been observed in this region by Prof. H. L. Callendar †, and peculiarities in the magnetic permeability when iron passes through this range of temperature have been described by Prof. D. K. Morris ‡. The residual magnetism of iron appears to be in a very sensitive state between 400° and 600° and behaves very uncertainly, but the thin line in the diagram may be taken as approximately the path which the magnetism follows on heating. On cooling the halt occurs at a lower temperature than on heating.

When cobalt is first heated, there is a small increase of magnetic intensity and it is not until about 250° that the

* Alloys Research Comm. 5th Report.

† Phil. Trans. Roy. Soc. 1887, p. 201.

‡ Phil. Mag. vol. xlv. 1897, p. 213.

diminution begins, while on cooling the magnetism rises to a value higher in the vicinity of 100° C. than what it is at the temperature of the room. These effects are, however, nearly obliterated on repeating the heating and cooling many times, although there is always a tendency for the intensity to be higher at about 100° on cooling than at lower temperatures. In other respects cobalt behaves regularly up to 750° C. The numbers which have been used in the construction of the curve for cobalt are mean values of experiments on electrolytic deposits of cobalt on copper and on platinum. Since the expansion of cobalt is intermediate between that of copper and platinum, it was considered justifiable to take the mean as the final result.

4. Experiments on the change of *residual* magnetism of nickel, iron, and cobalt over so extended a range of temperature do not appear hitherto to have been carried out, and it is useful to compare the results now arrived at with those which have been obtained in very intense fields by P. Curie *, Du Bois †, Honda and Shimizu ‡, and others. Curie's observations on iron were made in a field of 1300 c.g.s. units from air temperature to the critical temperature and beyond, and his curve agrees with the one for iron given above at the extremities, but is a little higher at intermediate points. There is no evidence of a halt at 400° to 600° .

Du Bois, using an optical method with ellipsoids of a dimension ratio of 30, has experimented upon nickel and cobalt as well as iron in intense fields, but has not carried the temperature beyond 300° C. His curves take rather an abrupt downward bend at temperatures beyond 200° , but in other respects are similar to those in Diagram 1. He does not give numerical results, but from the curves traced in his paper I have deduced the following approximate values of the temperature coefficient:

Temp.	Nickel.	Iron.	Cobalt.
0° – 100°	0.0005	0.00014	.00005
100° – 200°	0.0017	0.00033	.00015

The coefficients are largest in nickel and least in cobalt, and in all cases increase with the temperature.

Honda and Shimizu by means of the magnetometric method and employing ellipsoids having a dimension ratio of 20 have made experiments on annealed iron, nickel, and cobalt over a range of temperature which extended from

* *Ann. Chim. et Phys.* ser. 7, vol. v. 1895, p. 289.

† *Phil. Mag.* ser. 5, vol. xxix. 1890, p. 293.

‡ *Phil. Mag.* ser. 6, vol. x. 1905, p. 548.

—180° C. to 1200° C. The curves show that there is in low fields a maximum intensity for some intermediate temperature, but in the highest field employed 400 (c.g.s. units) this maximum disappears entirely in iron, is nearly obliterated in nickel, and becomes less pronounced in cobalt. There is little doubt that the curves would decline smoothly from the lowest to the highest temperature in very strong fields. From the curves traced by Honda and Shimizu I have constructed Table II., which shows again that the rate of diminution of magnetic intensity as the temperature rises is greatest in nickel and least in cobalt.

TABLE II.

Relation of Magnetic Intensity to Temperature. Honda and Shimizu's Observations in a field of 400 c.g.s. units.

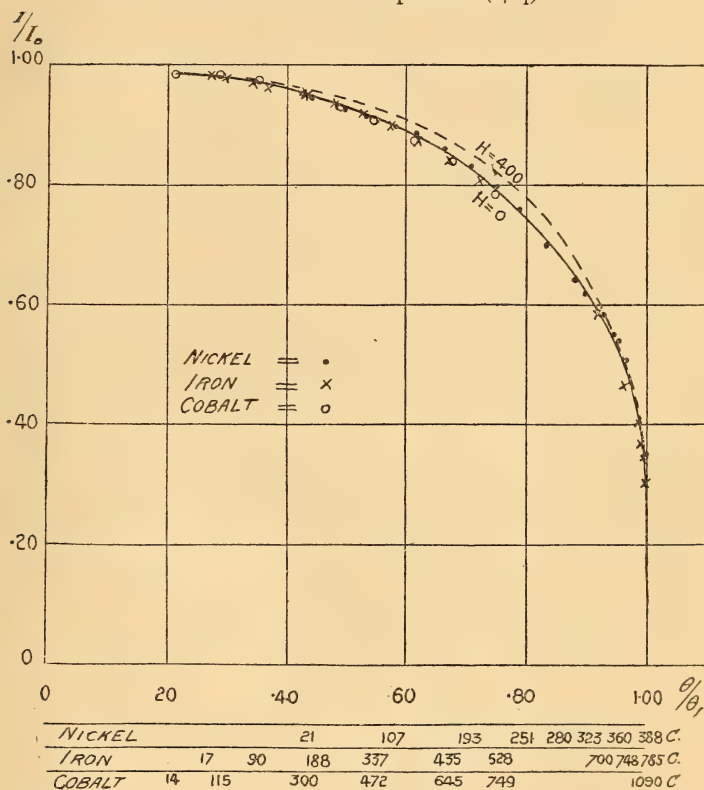
NICKEL.			IRON.			COBALT.		
Temp. C°.	θ/θ_1 .	I/I_0 .	Temp. C°.	θ/θ_1 .	I/I_0 .	Temp. C°.	θ/θ_1 .	I/I_0 .
0	·45	·95	0	·25	·98	0	·21	·98
50	·53	·91						
100	·62	·89	100	·35	·96			
150	·71	·84						
200	·79	·80	200	·44	·95			
250	·88	·67						
300	·96	·50	300	·54	·93			
			400	·63	·90			
			500	·73	·84	500	·58	·89
			600	·82	·76	600	·66	·88
			700	·92	·57	700	·73	·83
						800	·81	·76
						900	·88	·62
						1000	·96	·41

Critical temp.=320° C. | Critical temp.=785° C. | Critical temp.=1060° C.

5. The curves which have been traced in fig. 1 indicate that the behaviour of residual magnetism is of the same type for each of the three ferromagnetic elements. This similarity of type can be tested by plotting the fractional intensities on a reduced scale of temperature, in which the critical temperature is treated as unity and other temperatures as fractions

of the critical temperature. When this is done, the full curve in fig. 2 is obtained.

Fig. 2.—Relation of Fractional Magnetic Intensity (I/I_0) to Fractional Absolute Critical Temperature (θ/θ_1).



The ordinates are as before the fractional intensities, I/I_0 , and the abscissæ are the values of θ/θ_1 , where θ_1 is the absolute critical temperature.

Beneath this reduced scale of temperatures some of the corresponding values of the centigrade temperatures are given for the sake of easy comparison. In this diagram the cobalt values do not extend beyond $\cdot 75$ on the reduced scale, and the values for iron between $\cdot 75$ and $\cdot 90$ have been omitted.

When the separate points for each metal are laid down, they lie so closely together that it is possible to draw a smooth curve through *all* of them (the full line of fig. 2). Honda and Shimizu's * results, abstracted in Table II., when

* *Loc. cit.*

treated in the same way, lie very nearly on a single curve (the broken curve of fig. 2), which is very similar to the full curve in the same figure.

It follows from the concordance of the three curves of fig. 1, when plotted on a scale of reduced temperatures, that the change of fractional magnetic intensity for each of the ferromagnetic elements is the same for the same interval on this scale, or, that the coefficients of residual magnetism of the ferromagnetic elements in corresponding states are inversely proportional to the absolute critical temperatures.

6. This result is precisely the law for the change of density of liquids with variation of temperature, and it is of interest to inquire if the coefficients on a reduced scale of temperature are of the same order of magnitude.

Since the physical constants of water are well known, it may be selected as a typical liquid for comparison. The variation of its density with temperature has been determined by several observers, and according to Cagniard de la Tour its critical temperature is 390°C ., Hirn's value being rather higher. Adopting 390°C . or 663°A as the critical temperature, I have constructed Table III., in which the fractional density of water at different temperatures is placed side by side with the fractional magnetic intensity of nickel which has nearly the same critical temperature. To make the comparison easier, I have treated the density of water as 0.945 at 21°C ., which is numerically the same as the magnetic intensity of nickel at that temperature.

TABLE III.

Comparison of Fractional Intensity of Nickel and Fractional Density of Water.

Temp. $^{\circ}\text{C}$.	θ/θ_1 .	Nickel.	Water.	Difference. Nickel - Water.
21	.44	.945	.945	$\pm .00$
107	.57	.90	.91	$-.01$
135	.62	.88	.88	$\pm .00$
165	.66	.86	.85	$+.01$
193	.70	.84	.83	$+.01$
223	.75	.80	.79	$+.01$
250	.79	.76	.75	$+.01$
280	.84	.71	.71	$\pm .00$
310	.88	.66	.65	$+.01$
320	.89	.64	.63	$+.01$

Critical temperature of nickel = 388°C .
 „ „ of water = 390°C .

The differences which are given in the last column are so small that the correspondence may be treated as nearly exact.

Since the curve tracing the change of fractional density of water as a function of the reduced temperature is the same for other liquids in general, and is at the same time approximately the curve of change of fractional intensity of the ferromagnetic elements, it follows that the temperature coefficient of density of liquids and of magnetic intensity of the ferromagnetic elements in corresponding states are very nearly of the same magnitude.

7. Parallel with this result is the law of Curie that under a constant force the intensity of ferromagnetics at temperatures above the critical point is inversely proportional to the absolute temperature, and hence the temperature coefficient of intensity in the paramagnetic condition is the same as the temperature coefficient of density of a gas.

Thus the behaviour of the magnetic intensity of the ferromagnetic elements under variations of temperature bears a very close analogy to the behaviour of the density of a fluid under similar treatment.

8. A study of the passage of a fluid from the liquid to the gaseous state has led to the hypothesis that the constituent molecules mutually attract one another, but at the same time their thermal agitation plays the part of a repulsive force. In any given state there is equilibrium between these effects. By analogy Curie * suggests that the magnetic transformation from ferro- to paramagnetism may be due to the magnetic molecules passing from mutual attraction to a state of independence. This independence may arise in part from expansion, and in part from the enhanced energy of oscillation of bi-polar molecules. Any given magnetic state is then a state of equilibrium.

In a fluid the continuous change from one state to the other can be expressed most simply by Van der Waals's equation which recognizes the fact that there is a limit to the density of a liquid and that the molecules exert a mutual attraction equivalent to a pressure.

In magnetism it is generally agreed that there is a limit to magnetic intensity, and that the magnetic molecules exert a mutual attraction, and these are the counterparts of the two salient facts in Van der Waals's equation.

Thus the suggestive analogy between the gas laws and the laws of paramagnetism, first pointed out by P. Curie, is capable of extension and application to liquids and ferromagnetics, in so far as liquid density and ferro-magnetic intensity can be treated as functions of the temperature.

* *Loc. cit.*

IV. *Delta Rays*.—II. By NORMAN CAMPBELL *.

1. **T**HE following pages contain an account of experiments performed in continuation of those recently described under the same title †.

At the end of the former paper the question was discussed at some length whether the differences observed when the delta rays were excited in different metals were due to differences in the speed of the rays or to a difference in the reflecting powers of the metals for the rays. No certain decision was attained, though the evidence was on the whole in favour of the view that a difference in the speed had not been demonstrated. It was thought that the matter might be definitely settled, if in place of the metals soot were employed as one of the electrodes, since Baeyer ‡ has shown that this substance has practically no reflecting power. Hitherto attempts to use soot had been unsuccessful owing to uncertainties in the resulting measurements. These difficulties have now been overcome by certain slight changes in the apparatus and in the method of covering the electrodes with soot; in all important characteristics the apparatus is the same as in the experiments described previously. In the later observations an electrometer was used in place of the electroscope as the indicating instrument of the measuring system. In so far as there is conflict between the present experiments and those already described, I am inclined to attribute greater weight to the more recent work.

2. The measurements which had been made previously with the electrodes covered with aluminium, copper, silver, and gold were repeated and similar measurements made with the electrodes covered with soot. The results are given in Table I. and fig. 1. The significance of the numbers in the columns marked +, —, and "sum" is the same as that of the numbers in the corresponding columns of Tables 3–5 of the previous paper. In fig. 1 (p. 48), which is similar to fig. 3 of the previous paper, the results of the "sum" columns are plotted.

A comparison with the previous work will show that the general trend of the curves for aluminium, copper, silver, and gold and the general relations between the curves is the same as in the previous work. But the results are not completely identical; it had been found before that very slight

* Communicated by the Author.

† Phil. Mag. Aug. 1911, p. 276.

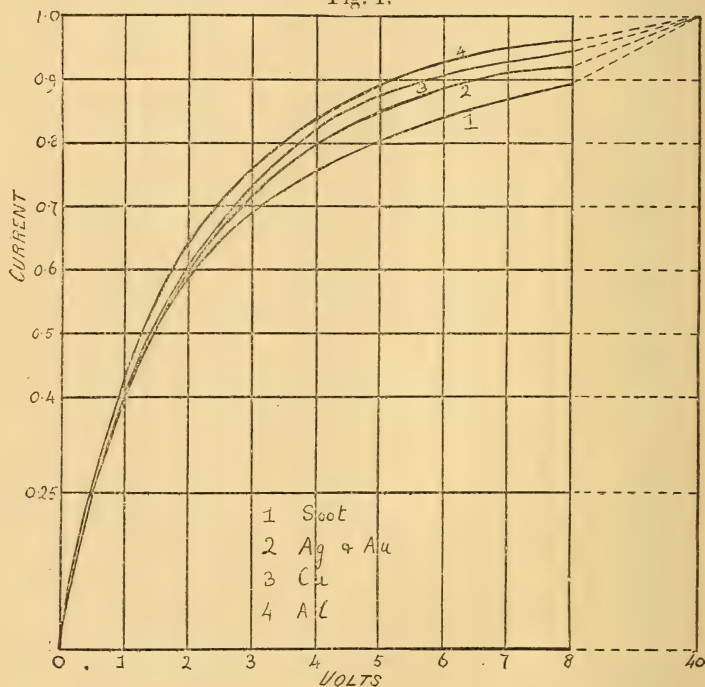
‡ Baeyer, *Phys. Zeit.* x. p. 176 (1909).

TABLE I.

	Soot.	ALUMINIUM.	COPPER.	SILVER.	GOLD.
	+ - Sum.	+ - Sum.	+ - Sum.	+ - Sum.	+ - Sum.
V=0	+0.56	+0.54	+0.41	+0.45	+0.51
V=0 (magnet)	+0.62	+0.81	+0.76	+0.76	+0.76
V=40	0.257 0.253 0.510	0.261 0.264 0.525	0.257 0.205 0.462	0.253 0.189 0.442	0.264 0.214 0.478
V= $\frac{1}{2}$	.241 .245 .244	.268 .265 .266	.252 .230 .243	.254 .206 .232	.277 .197 .240
1	.392 .400 .398	.430 .416 .423	.408 .380 .399	.427 .360 .397	.414 .360 .390
2	.582 .594 .587	.650 .643 .643	.618 .581 .605	.650 .535 .599	.600 .595 .598
3	.670 .705 .686	.763 .758 .759	.730 .698 .720	.740 .699 .718	.710 .716 .710
4	.740 .771 .756	.843 .830 .836	.833 .790 .820	.820 .768 .792	.790 .806 .797
6	.829 .850 .840	.932 .925 .927	.915 .884 .905	.890 .879 .882	.881 .904 .889
8	.895 .895 .896	.965 .963 .968	.960 .932 .945	.933 .931 .929	.919 .932 .923
40	1.000 1.000 1.000	1.000 1.000 1.000	1.000 1.000 1.000	1.000 1.000 1.000	1.000 1.000 1.000

changes in the apparatus made it impossible to reproduce accurately the results of a series of measurements; these results seem to some extent a function of the exact form of

Fig. 1.



the apparatus. It is to be noted that the curve for soot is considerably flatter than that for any of the metals. Indeed the difference between soot and the other materials is really greater than appears from the figure; for in the figure all the values of the current are expressed as ratios of the current for a potential difference of 40 volts, and, while the current for the metals is completely saturated for that potential difference, the current for soot does not become saturated until the potential difference is nearly 80 volts. If the curve for soot were, like that for the metals, referred to the maximum ordinate as unit, it would appear even flatter.

The further discussion of these observations will be postponed for the present.

3. Experiments were next tried, similar to those described in § 15 of the previous paper, in which the lower electrode (A) was covered with soot, while the upper electrode (B)

was covered successively with aluminium, copper, silver, and gold. The results are plotted in fig. 2 (p. 50), where the ordinates now represent the *absolute* values of the current, expressed in the units described in the previous paper, and not the ratios of the current to the maximum current. In Table II. the results are given in a form similar to that of Table I., except that the "sum" column is omitted as having no significance when the electrodes are of different materials.

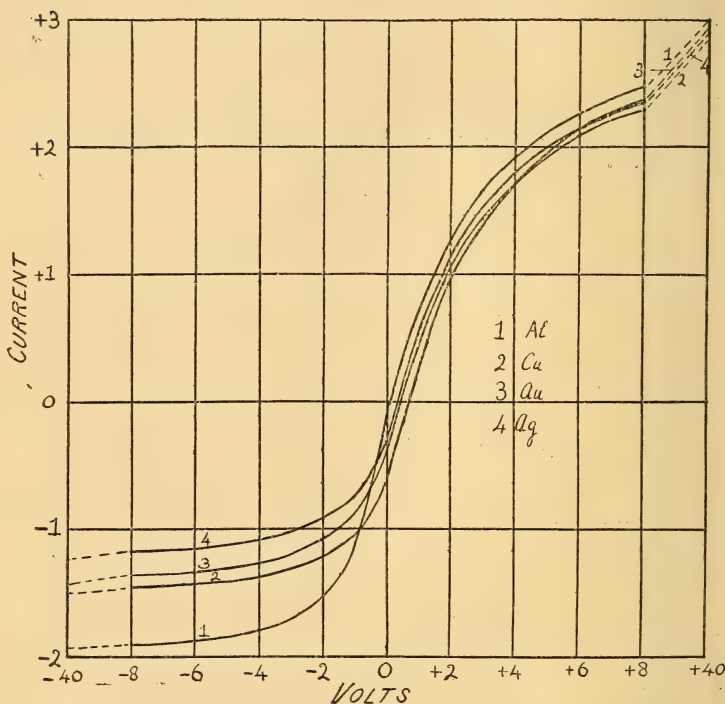
TABLE II.

	ALUMINIUM.		COPPER.		SILVER.		GOLD.	
	+	-	+	-	+	-	+	-
V=0	-·009		-·064		-·029		-·040	
V=0 (magnet)...	-·065		-·056		-·055		-·056	
V=40	0·313	0·184	0·360	0·086	0·321	0·093	0·328	0·103
V= $\frac{1}{2}$	·144	·321	·127	·296	·137	·269	·147	·285
1	·252	·582	·259	·478	·271	·484	·269	·466
2	·441	·788	·449	·675	·458	·645	·452	·650
3	·559	·881	·562	·768	·576	·763	·569	·779
4	·649	·918	·659	·861	·654	·828	·654	·839
6	·757	·973	·754	·909	·766	·914	·762	·907
8	·824	·994	·838	·949	·829	·935	·829	·942
40	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000

It may be noted in passing that additional evidence was obtained for the conclusion, given in the previous paper, that the quality of the delta rays excited in a substance is independent of the speed of the alpha rays exciting them. For most of the observations given in Table II. were repeated with the polonium plate covered by a layer of aluminium foil equivalent in its stopping power to about 3 cm. of air. The presence of the foil increased all the values given in the table below the thick line by about 50 per cent.—the increase is doubtless due to the greater ionizing power of the alpha ray towards the end of its range—but it did not change the ratio of those values to any perceptible extent. The form

of the curve was quite unaltered by the presence of the absorbing layer.

Fig. 2.



4. A mere glance at the curves in fig. 2 will show at once that the simple theory given at the beginning of the previous paper is quite inadequate to explain the results obtained when one of the electrodes is covered with soot. And, since it is only on the basis of that theory that any deductions as to the speed of the rays can be made from an examination of these measurements, all conclusions which have been suggested as to the speed, and many conclusions on other points also, are rendered dubitable.

For, according to this theory, the upper (+) portion of the curve should represent the properties of the rays emitted by the upper electrode (B), while the lower (-) part should represent the properties of the rays emitted by the lower electrode (A). But in these experiments the material covering A, soot, was the same in all cases, while the material covering B varied. It would be expected then that the lower part of the curve should be the same in all cases,

while the upper part varied. Again, since the curve with both electrodes covered with soot is flatter than that with the electrodes covered with metal, it would be expected that the lower half of the curve would be flatter than the upper half. Both expectations are completely falsified; the most casual examination shows that if the curves are to be divided into two halves, one of which resembles more the curve for soot and the other resembles more the various metals, it is the upper half which must be associated with the soot and the lower half which must be associated with the metals. No more striking refutation of the theory could possibly be obtained.

5. Now the theory which has been employed hitherto was based upon the fundamental assumption that, when the electrodes were at the same potential, all the rays emitted by one were received by the other; and that the effect of raising A (or B) to a positive potential relative to B (or A) was merely to prevent some of the rays emitted by A (or B) from reaching B (or A). If this assumption is correct, it is clear that the part of the curve corresponding to positive potentials of A (or B) must be determined by the speed of the rays leaving A (or B). But it was pointed out in the last paper that it is possible that the electrodes possess so high a reflecting power for the rays incident upon them that the variation of the number of rays received by them is determined less by a variation in the number of rays which can cross the space between the electrodes under different electric fields than by the number which reach the electrode, but are reflected by it, under different electric fields. In this case, since the rays emitted by A are reflected by B, the part of the curve corresponding to positive potentials on A would be determined less by the properties of A than by the properties of B. Accordingly it appears at first sight as if the results which have just been recorded might be explained on the assumption that the influence of reflexion upon the form of the curve is so important as to mask completely any effects due to the direct stopping of the rays by an opposing field.

There are many objections to this view which will probably occur at once to the reader. Most of them rest upon improbabilities concerning actions of which we know very little, and are not therefore conclusive, though their accumulated weight is considerable. But one objection appears to me quite insuperable, and it alone will be put forward.

It is known from Baeyer's work that soot shows very little reflexion. Accordingly the curve obtained when both

electrodes are covered with soot cannot be greatly influenced by reflexion ; its form must be determined on our present view by a direct stopping of the rays by the opposing electric field. But it has been noted that the current with soot-covered electrodes is not saturated until a potential difference of more than 40 volts is applied. The only possible interpretation of this fact consistent with our present hypothesis is that some of the rays emitted by soot have a speed corresponding to a potential difference greater than 40 volts. Now, when A is covered with soot and B with aluminium, we must suppose that rays with a speed corresponding to 40 volts are leaving A and striking B. Unless *all* these rays are reflected from B (a supposition for which Baeyer's work gives no warrant) the current obtained by raising A to a positive potential cannot become saturated until that potential is great enough to prevent the rays reaching B at all, that is, until it is greater than 40 volts ; but experiment shows that the current is saturated when the potential of A is +10 volts.

Or again, it will be seen that the positive branches of the curves when A is covered with soot are practically identical whether B is covered with aluminium, copper, silver, or gold. Even on the reflexion hypothesis this result implies that the speed of the rays from those four metals is practically the same, for the reflecting power undoubtedly depends upon the speed of the incident rays. But, if the speed of the rays from these four substances is the same, it is utterly unjustifiable to suppose that the speed of the rays from soot is very different ; and, if the speed of the rays from aluminium (say) is the same as the speed of the rays from soot, how comes it that the current with aluminium electrodes is saturated by 40 volts when the rays from soot undoubtedly include some which have a speed greater than that corresponding to 40 volts? I conclude that the hypothesis of reflexion together with the simple theory of the last paper is quite incapable of accounting for the results obtained when one of the electrodes is covered with soot.

6. It is easy to frame an alternative hypothesis for this case. The main feature to be explained is that the branch of the curve corresponding to positive potentials on B represents the properties of A and not the properties of B. Hitherto we have supposed that, in the absence of an electric field, the delta rays leave readily the electrode at which they are generated and that the action of the field is to prevent some of the rays leaving it. If we make exactly the contrary supposition, that in the absence of a field very few of the

rays leave the electrode and that the action of the field is to drag some of the rays out of the electrode at which they are generated, the main feature is explained. For, if the effect of positive potentials on B is not to stop the rays from B generated in B from reaching A, but to aid the rays generated in A in reaching B, then it is clear that the branch of the curve corresponding to potentials positive on B must be determined by the properties of A and not by the properties of B.

In the case of soot this new hypothesis has considerable *a priori* probability. For Baeyer has shown that the reflecting properties of a material depend on the condition of its surface rather than upon its chemical nature. For instance, metallic platinum is a good reflector, platinum-black a bad reflector. It is natural, therefore, to suppose that the absence of reflexion is due to the entanglement of the electrons in the rough surface of the material, and that the slow-moving electrons generated at the surface of the soot-covered electrode will not be able to escape from it completely unless they are aided by an electric field. We should expect, as we find, that it would require a greater electric field to drag a given proportion of the rays out of a surface of soot than out of a metallic surface, and, consequently, that the curve in fig. 1 for soot should be flatter than those for metals.

7. When one of the electrodes is covered with soot some explanation of this nature appears absolutely necessary. The question next arises whether it can be applied to explain the differences between the curves obtained with different metals. Since no metal surface is perfectly smooth and no metal is a perfect reflector for slow-moving electrons, it is to be expected that the results with metals will also be affected to some extent by the cause which has been suggested in connexion with soot. It is true that the curve for aluminium is always steeper than those for the other metals, whereas Baeyer found the reflecting power of that metal to be somewhat lower than that of the others, but there may be causes, such as electric fields in the surface, which would affect electrons generated in the surface but not electrons moving up to the surface and reflected by it. On the other hand, the supposition that the form of the curves is determined largely by the condition of the surface of the electrodes would readily explain the difficulty which has been experienced in reproducing accurately a series of readings after small alterations have been made in the apparatus.

On these grounds it seems to me much more probable that the differences obtained with electrodes of various

materials are due to differences in the ease with which the electrons escape from the surfaces of those materials, than that they are due either to a difference in the speed of the electrons generated or to differences in the reflecting powers of the surfaces. But the form of the curve relating current to potential difference cannot be determined *wholly* by the action of the field in aiding the electrons to escape, unless the initial speed of the electrons is so low that, in the absence of a field, none of them escape. Now it would simplify very considerably our ideas of the mechanism of ionization by alpha rays if it could be imagined that the initial speed of the delta rays was practically zero ; we might then suppose that the action of the alpha particle in passing through an atom was merely to neutralize temporarily the electric forces in its interior and so to allow to escape electrons which were previously held by those forces within the atom ; the escaping electrons would be similar to the "free" electrons in metals and would have velocities corresponding to a potential difference of a few hundredths of a volt, determined by the temperature of the substance. Such an hypothesis appears to me very attractive and it would explain quite adequately the general form of the curves relating current between the electrodes to their potential difference which have been given in this paper and by other investigators, if the supposition were added that the liberated electrons could not escape from the surface except by the aid of an electric field, the magnitude of which is determined by the nature of the material and the condition of its surface.

8. But, unfortunately, there are considerations which make it impossible to accept immediately this simple and attractive hypothesis. These considerations are based upon the magnitude of the potential difference between the electrodes for which the current between them becomes zero.

If it were possible to obtain a single insulated electrode emitting only delta rays surrounded by another electrode which emitted no rays, the potential to which the first electrode would rise automatically, which is the same as that for which there is no current between the electrodes, would be equal to that corresponding to the speed of the delta rays emitted by it. This principle has been applied, of course, to the measurement of the speed of the electrons liberated by light from various substances. However, in the case of delta rays it is impossible to fulfil this condition ; for, in the first place, there is the charge carried by the alpha rays which excite the delta rays to be taken into consideration, and, in the second place, the enclosing electrode is always

emitting delta rays which will be attracted to the insulated electrode as soon as its potential rises. It is easy to see that, if the alpha rays are emitted from the insulated electrode, both these causes tend to decrease the potential to which the insulated electrode will rise and accordingly the potential difference for which the current is zero will give us a minimum estimate for the speed of the rays. Experiments of this kind have been carried out by Ewers *, Logeman †, and Hauser ‡; the first-named gives 1.9 volt as the highest potential to which the insulated electrode was seen to rise, from the curve given by the second it would appear that the current was zero for about 1.0 volt, while in the experiments of the third the corresponding potential difference would appear to be about 2.6 volts. The arrangements in my own experiments are less well suited to give information on this point, but a little consideration will show that a minimum estimate of the potential corresponding to the speed of the rays is given by the potential difference between the electrodes for which the current has the same value as it has when the potential difference is zero and the magnetic field is applied. This potential difference is never greater than 1 volt. It will also be seen that, if the delta rays possessed no velocity of their own, the current corresponding to " $V=0$ " must always lie between zero and the current for " $V=0$ (magnet)"; this condition is by no means always fulfilled.

It seems necessary to conclude therefore that, unless current can be conveyed between the electrodes by some agency other than the alpha and delta rays—and no such agency can be suggested—the initial velocity of the delta rays must be taken as at least that corresponding to a potential difference of 3 volts.

But if the delta rays possess so large an initial speed, the form of the branch of the curve for positive potentials on B must be affected to some extent by the speed of the rays emitted by B; for part of the change of the current in the region between zero and the potential difference corresponding to the speed of the rays must be due to a direct stopping of the rays by the field. How far the effect of direct stoppage of the rays from B will be masked by changes due to the dragging out of electrons from A it is impossible to say. But an examination of the + columns in Table II. shows no sign whatever of any systematic difference when B is covered by different materials; so far as the evidence goes, it shows

* Ewers, *Phys. Zeit.* vii. p. 148 (1906).

† Logeman, *Proc. Roy. Soc. A.* lxxviii. p. 262 (1906).

‡ Hauser, *Phys. Zeit.* xii. p. 466 (1911).

that the speed of the rays from different materials is the same, though it cannot be estimated what difference in the speed might escape detection.

9. We may sum up the results of the foregoing discussion as follows :—

A great part of the change in the current due to a change in the field between the electrodes is due to the dragging out of the electrodes of delta rays generated in them which were previously unable to escape. It is therefore quite illegitimate to attempt to deduce from the potential difference necessary to saturate the current any information as to the maximum speed of the delta rays. Saturation is attained, probably, when the field is sufficient to drag all the electrons out of the electrodes, not when it is sufficient to prevent the electrons crossing the space between the electrodes in opposition to the forces of the electric field. Experiments such as these can give no information as to the maximum speed of the rays. On the other hand an examination of the form of the curves for small potential differences may give a minimum estimate of that speed. The work of other investigators leads to the conclusion that that speed is not less than that corresponding to a potential difference of 3 volts. The observations described here seem to prove that the properties of the delta rays are quite independent of the speed of the alpha rays exciting them, and lend no support whatever to the view that the speed of the delta rays depends on the material from which they are emitted. The experiments are quite consistent with the view that the speed of the delta rays is a universal constant*.

10. So far as we have been concerned only with the quality of the delta rays. The conclusions which we have reached have also important bearings on the results which were given in the previous paper as to their quantity, more especially on the question of the relative amounts of "incident" and "emergent" radiation.

Let Z be the current between the electrodes for " $V=0$ " and Z' that for " $V=0$ (magnet)"; let $M+$ be the maximum saturated positive current and $M-$ the maximum saturated negative current. Then on any view of the speed of the delta rays, if the effect of the magnet is to prevent any of the delta rays from one electrode reaching the other—reasons will be given later for thinking that this condition is not

* It is to be noted that this conclusion has been advanced by Wertheimer recently (*Phys. Zeit.* xii. p. 411, 1911), and that the reduction in the estimate of the speed of the rays which has been suggested is favourable to his views.

always fulfilled,—E and I, respectively the currents representing the whole of the emergent and the whole of the incident radiations, are given by

$$\begin{aligned} E &= (M -) - Z' \} \cdot \cdot \cdot \cdot \cdot (1) \\ I &= (M +) - Z' \} \end{aligned}$$

On the other hand, if the simple theory of the last paper were correct, and, in the absence of an electric field, all the rays from one electrode were received by the other, it was shown that

$$\begin{aligned} E &= Z - (M +) \} \cdot \cdot \cdot \cdot \cdot (2) \\ I &= Z - (M -) \} \end{aligned}$$

It is to be noted that, on these suppositions, if the emergent and incident radiations are equal, we should have

$$Z' = Z.$$

It was noted in the last paper that the estimates of E and I given by (1) and (2) do not, in general, agree; and the question arises which of the two is the more reliable. In the last paper, complete confidence was placed in the simple theory and the estimates given by (2) were accepted. This choice was made because, in order to interpret the results so as to give information as to the quality of the rays, it was necessary to reckon both branches of the curve from Z as zero; it was natural to reckon from the same point when estimates of quantity were to be made. But the arguments of the foregoing paragraphs have shown that the theory of the last paper is absolutely unreliable and that, accordingly, no trust can be placed in estimates of E or I based on (2). At least in cases when the surface of the two electrodes are different, Z is not the current which flows when all the rays from one surface strike the other; for, if the rays can escape more easily from one surface than the other, the electrode from which the rays can more easily escape will lose more electrons than it receives, even if the number of rays generated is the same for both electrodes.

This point is strikingly illustrated by the curves of fig. 2. It will be observed that Z is very much smaller than Z', but it does not necessarily follow that the quantity of the rays generated at the two electrodes is different. For we imagine that the rays leave a metal surface much more easily than a surface of soot; and, when there is no difference of potential between the electrodes, A will be receiving from B more electrons than it gives up to B. Accordingly, as is found, the current received by A will be less algebraically than it

is when the magnetic field acts and the electrons cannot pass from one electrode to the other. An anomaly which has hitherto been left unnoticed is thus readily explained. According to the original theory the number in the third row of the “—” column of Table II. should represent the quantity of the incident radiation. This number is different for each of the materials, although, since the incident radiation is excited at the soot electrode in each case, it would be expected that it should be the same. However, if we estimate the incident and emergent radiations by (1), this anomaly disappears. We obtain the following figures:—

Aluminium—soot ...	$E=0.258$; $I=0.250$ *.
Copper—soot	$E=0.216$; $I=0.249$.
Silver—soot	$E=0.177$; $I=0.248$.
Gold—soot	$E=0.199$; $I=0.244$.

It will be seen that the incident radiation, which proceeds from the soot, is the same in each case approximately ; while the emergent radiation, which proceeds from the metal, is different. It appears then that in this case it is more satisfactory to estimate the emergent and incident radiations by (1).

Turning now to the results when both electrodes are of the same material we get the following results according as the quantities are calculated by (1) or (2):—

By (2) Aluminium ..	$E=0.261$	$I=0.264$
Copper	$E=0.257$	$I=0.205$
Silver	$E=0.253$	$I=0.189$
Gold	$E=0.264$	$I=0.214$
Soot	$E=0.263$	$I=0.268$
By (1) Aluminium..	$E=0.291$	$I=0.234$
Copper	$E=0.240$	$I=0.222$
Silver	$E=0.220$	$I=0.222$
Gold	$E=0.239$	$I=0.239$
Soot	$E=0.262$	$I=0.269$.

These results are not entirely satisfactory, for in some cases one method of calculation and in other cases the other makes the incident and emergent radiations equal. The only case in which both methods make the radiations equal is that of soot. But at any rate there is no evidence that the incident

* It has been noted that the curves for soot are not completely saturated until a potential difference of 80 volts is employed. The numbers used for calculating the total quantity of radiation from soot are those for 80 volts and not those given in Table II. in the row “ $V=40$.”

is greater than the emergent radiation, as was asserted in the previous paper. If the results of that paper are calculated according to (1), it appears that there also the radiations are nearly equal, the emergent (and not the incident) showing a slight preponderance. The results of method (1) certainly inspire the greater confidence, for those of method (2) depend entirely upon the value for " $V=0$ "; it has been already noted that the values of this point are much more variable than those of any other, and the hypotheses advanced in the foregoing paragraphs would tend to account for the variability. According to these hypotheses the position of that point is largely influenced by differences in the surface conditions, which determine the ease with which the electrons can escape. In these circumstances there seems no evidence left for the view that the incident is greater than the emergent radiation, or indeed for the view that the two are not equal.

12. One curious point, which is difficult to explain, and while unexplained renders somewhat uncertain all conclusions as to the quantity of the radiation, must be mentioned. It will be noted that the values calculated by (1) for the emergent radiations from the various metals when the lower electrode is covered with soot do not agree with the values calculated by the same method of the same quantity when both electrodes are of the same material. They agree rather with the calculated values of the *incident* radiation according to (2) when both electrodes are the same. The only explanation I can suggest is that, when the electrodes are the same, the value for " $V=0$ " and not that for " $V=0$ (magnet)" gives the value for the current in such circumstances that none of the rays from one electrode strike the other; such would be the case if the rays were unable to escape at all from a metal surface without the aid of a field. But in that case it is difficult to see why the application of the magnetic field should change the current. It is possible also that the discrepancy is connected in some way with the fact that the electrode B consisted always of a very thin sheet of the material, while A was covered with a much thicker sheet. Hauser (*loc. cit.*) has concluded that the delta rays have an appreciable penetration, and that the full amount of them is not emitted from a sheet until it has reached a considerable thickness. The evidence for this view seems inconclusive, but in the light of these observations it cannot be rejected summarily. It might explain the fact that it appears from these experiments as if the total amount of delta radiation varied somewhat with the material

in which it is excited, while the experiments described in the last paper undertaken specially to test the point showed that the radiation from all materials was the same within a few per cent.

13. One more conclusion asserted in the last paper must be withdrawn. It was stated that the quantity of delta rays emitted by a plate covered with polonium was more than that emitted by any other electrode on which the alpha rays from the polonium fell, and that, therefore, there must be true delta rays emitted by the polonium itself*. It is now seen that the second part of this statement is not a necessary consequence of the first. For, when the alpha rays from the polonium plate fall on any other electrode, only those delta rays can escape which are ejected towards the surface of that electrode; but, since the active material is in a very thin and probably discontinuous film on the surface of the plate, it is possible that not only the rays generated in the polonium film, but also some of those generated in the plate on which it is supported can escape under the action of an electric field tending to drag them out. The apparently greater emission of delta rays from the active plate itself may be merely due to the fact that in this case the rays generated over more than a hemisphere can reach the opposite electrode.

14. In view of the uncertainty which appeared to attach to all the results obtained by the method of investigation hitherto employed, an attempt was made to devise some more satisfactory means of investigating the properties of the delta rays. It was thought that possibly information might be yielded by the study of ionization by collision, using alpha rays as a primary ionizing agent. A good many observations have already been made in this direction, but an account of the results will be left for a future paper. It need be only recorded here that the evidence, so far as it goes, is still distinctly against the view that there is any difference in the speed of the rays generated in different materials, and that it appears very improbable that the speed of those rays can be, as some investigators have concluded, nearly as great as that corresponding to the potential difference of 25-30 volts which Townsend gives as the minimum speed at which an electron possesses sufficient energy to form an ion. The conclusions then agree so far

* The same conclusion has been advanced by Hauser (*loc. cit.*), but all his measurements of quantity as well as quality are somewhat doubtful in the light of the considerations put forward in this paper.

with those of the work described in this and the previous paper.

15. Some explanation is necessary why no attempt has been made to use the magnetic method of determining the velocity of the rays which has been used by Ewers and Hauser (*loc. cit.*). The reason is that the examination of the work of those authors, together with a few observations which I have made, have led me to a complete mistrust of that method as a means of getting accurate results.

The theory of the method is given very completely by J. J. Thomson in his 'Conduction of Electricity through Gases' (2nd ed.) sections 57, 58 *. The rays are supposed to be emitted from one or both of two parallel plates, in the space between which a magnetic field H is established with its lines parallel to the plane of the plates. The measurements can be made in two ways. In the first a magnetic field is established strong enough to prevent the rays crossing between the electrodes when they are at the same potential difference, and then the potential difference is increased and the value of the electric field found necessary to make, first some, and then all, of the rays cross. If X_1 and X_2 are the two values of the field corresponding to these two conditions, and v is the velocity of the rays

$$v = \frac{1}{2} \frac{X_2 - X_1}{H}; \quad e/m = \frac{X_1 + X_2}{H^2 d}.$$

In the second method an electric field X , strong enough to make all the rays cross between the electrodes, is established, and then H is increased from zero until first some and then all of the rays are prevented from crossing. If H_1 and H_2 are the two values of the field corresponding to these two conditions

$$v = \frac{X(H_2 - H_1)}{H_1 H_2}; \quad e/m = \frac{2X}{H_1 H_2 d}.$$

It is clear that this method must fail unless all the rays have the same speed, or unless this speed is so small compared with X/H that it may be put equal to zero. For the values of X_1 and H_2 are determined by the speed of the fastest rays, whereas X_2 and H_1 are determined by the speed of the slowest rays. Since then there is no evidence that the rays are homogeneous, considerable doubt attaches to the method from the start.

* I am unable to follow completely the methods by which the authors named interpret their results. The conclusion given here, based on Thomson's theory, is rather different from that at which they arrive.

Further limitations must also be noticed. Since we have concluded that an increase in the electric field between the electrodes may change the current by increasing the number which are dragged out of the electrode, it is clear that the method by which the magnetic field is kept constant and the electric field is varied is illegitimate. This method was employed by Ewers*. On the other hand, it is obvious that no rays must be emitted from any part of the apparatus except the parallel plates, or at least from none whence the rays can reach the electrodes by travelling *along* (and not *across*) the magnetic field; for if there are such rays they will not be affected to the same extent by the magnetic field. Now in Hauser's experiment one electrode is completely surrounded by the other and delta rays are excited from all parts of both electrodes which the alpha rays can reach; accordingly Hauser's results must also be viewed with considerable suspicion.

If, notwithstanding these objections, we calculate the values of v and e/m given by the experiments of these authors, we obtain the following results:—

$$\begin{aligned} \text{Ewers:} \quad d &= 1.7; H = 20; X_2 = 79 \times 10^8; X_1 = 0, \\ \text{and} \quad v &= 2.0 \times 10^8; e/m = 1.16 \times 10^7. \end{aligned}$$

$$\begin{aligned} \text{Hauser:} \quad d &= 0.08; X = 122 \times 10^8; H_1 = 50; H_2 = 600, \\ \text{and} \quad v &= 2.2 \times 10^8; e/m = 1.0 \times 10^7. \end{aligned}$$

It will be observed that there is considerable agreement between the results, but that the value deduced for e/m is much smaller than the 1.77×10^7 which is now accepted.

Owing to the objection which has been raised as to the heterogeneity of the rays, it is perhaps more satisfactory to assume the value for e/m , and then to calculate the maximum and minimum values of v given by the two conditions. In this way we obtain:—

$$\begin{array}{llll} \text{Ewers:} & v \text{ (max.)} & = 3.0 \times 10^8 & \text{corresponding to 25.5 volts,} \\ & v \text{ (min.)} & = 1.0 \times 10^8 & \text{,, ,, 2.8 ,,} \\ \text{Hauser:} & v \text{ (max.)} & = 4.0 \times 10^8 & \text{,, ,, 45.0 ,,} \\ & v \text{ (min.)} & = 2.1 \times 10^8 & \text{,, ,, 12.4 ,,} \end{array}$$

These numbers are not consistent amongst themselves, nor

* Ewers employed a grid over his active materials in order to prevent rays from affecting the experiment unless they were emitted within a certain angle. He was unaware of the existence of the secondary delta rays; if these are taken into account it appears that rays must have been emitted in all directions from the surface of his grid. The allowance made for this fact accounts for part of the discrepancy between the values calculated by him and those calculated here.

do they accord in the least with the evidence derived from the study of curves of the nature given in this and the previous paper. There is no evidence from the relation between current and potential difference of the presence of rays with a speed so high as that corresponding to 25 volts, or of the absence of any rays with a velocity less than 2.8 volts.

When the amounts of the incident and emergent radiations were under consideration above, a doubt was expressed whether the magnetic field really prevented all the rays from one electrode reaching the other. It is to be noted that if the magnetic field were not everywhere accurately parallel to the plane of the electrodes, but possessed a component perpendicular to them, no increase in the magnitude of the field would produce the condition considered in Thomson's theory. The authors who have been quoted give an account of no investigation designed to test this point, although it is notably hard to obtain a homogeneous magnetic field over any considerable area. In my own apparatus, many lines of argument showed that the field between the plates was not strictly homogeneous and on this account, as well as on account of the discrepancies exhibited by the results of previous workers, an attempt to obtain any quantitative measurements was abandoned. Some observations were made, however, on the effect of the magnetic field on the current when different materials were used as electrodes, with the object of detecting any difference in the speed of the rays emitted. The results are not, for the reasons given, very conclusive, but as far as they went they were purely negative. No difference in the effect of the magnetic field could be detected when the material of the electrodes was changed, so long, of course, as both electrodes were of the same material.

Summary of Results.

The main portion of the paper is devoted to the destruction of the conclusions given as the result of experiments described in a previous paper under the same title.

It is concluded that experiments on the relation between the current and the potential difference between the electrodes can give very little information as to the speed of the delta rays emitted from the electrodes. Examination of the form of the curve when the potential difference is small may possibly give a minimum estimate of the speed of the rays; this minimum estimate, based on the work of other observers,

is given as about that corresponding to a potential difference of 3 volts. Examination of the form of the curve when the potential difference is so large that the current is nearly saturated probably does not give any information as to the maximum speed of the rays.

It is shown that there is considerable evidence that the speed of the rays is independent of the speed of the alpha rays by which they are excited. Such evidence as there is—but there is not very much—shows that the speed is also independent of the material from which the rays are emitted. It can be confidently asserted that there is no such difference between the secondary delta radiation from aluminium and gold as there is, for example, between the secondary Röntgen radiations from those metals.

It is also difficult to compare with any certainty the quantity of the emergent and incident radiation. A consideration of the experiments described in this paper shows that the conclusion advanced in the previous paper that the incident radiation is greater than the emergent is quite unjustified; there is no evidence that the amount of the two radiations is not equal.

The conclusion that polonium emits a true delta radiation, which is not merely a secondary radiation excited by the alpha rays, is also withdrawn.

In the final paragraphs of the paper considerations are put forward to show that the magnetic method of measuring the speed of the rays, at any rate in the form in which it has been used by previous observers, is as untrustworthy as the method which has been attempted in these papers.

The University, Leeds.

July, 1911.

V. *A Deduction of the Effects of Uniform Translatory Motion, from the Electrical Theory of Matter, without the Employment of a Transformation of the Electromagnetic Equations.* By W. F. G. SWANN, D.Sc., A.R.C.S., Assistant Lecturer in Physics at the University of Sheffield *.

IT is generally recognized that when a piece of matter is set in motion with velocity v , it contracts in the ratio $\left(1 - \frac{v^2}{C^2}\right)^{\frac{1}{2}}$ where C is the velocity of light. This fact has been explained by Sir Joseph Larmor, and by Lorentz, as following from the electrical constitution of matter, and other

* Communicated by the Author.

points of interest have been brought to light in the examination of the question, one of the most curious of which is the conception of local time. These ideas originally found their basis in the fact that the electromagnetic equations when transformed to a system of moving axes, reverted to the type for a system at rest. The reasoning is somewhat of an abstract nature, and it seems desirable for deeper insight into the matter, to deduce the contraction, together with the other results associated with it, by a method which follows more closely our ordinary concrete methods of reasoning. It is with this object that the present paper has been written.

On the electromagnetic view, a piece of matter consists entirely of an assemblage of positive and negative electrons, in a state of stationary motion, and while the electrons may be collected into groups and sub-groups which we call molecules and atoms, they nevertheless as a whole form one complete system.

The resulting effects produced by imparting a uniform translatory motion are most easily arrived at for the particular kind of system in which all the electrons are at rest, when the system as a whole is at rest, *i. e.* the electrons in the system at rest are considered absolutely devoid of motion, but difficulty here arises owing to the impossibility of such a system being in equilibrium, unless constraints are applied at the boundary; we shall, however, consider this case first, and shall overcome our scruples with regard to the equilibrium of the system by stating the problem to be proved as follows.

"If the electrons of a system are absolutely at rest, and are in equilibrium, constraints being applied to the electrons at the boundary to prevent the system from collapsing, then when this system is set in motion parallel to the axis of x with velocity v , it can again assume a state of equilibrium, if suitable constraints are applied at the boundary, by shrinking parallel to the axis of x so that the difference of the x coordinates of any pair of electrons is reduced in the ratio $(1 - \frac{v^2}{C^2})^{\frac{1}{2}}$."

Now it is a well-known fact that a point charge of strength e when moving with velocity v parallel to the axis of x produces on unit charge at rest in the æther, a force whose components X, Y, Z are given by

$$(X, Y, Z) = (X_0, Y_0 + v\gamma, Z_0 - v\beta)$$

where α, β, γ is the magnetic force due to the motion of the

Phil. Mag. S. 6. Vol. 23, No. 133. Jan. 1912. F

point charge, and X_0, Y_0, Z_0 is the part of X, Y, Z which is derivable from a potential Φ of the form

$$\Phi = \frac{eC^2\epsilon^{-1/2}}{(\epsilon x^2 + y^2 + z^2)^{1/2}},$$

the point charge being taken momentarily as origin and ϵ being written for $\left(1 - \frac{v^2}{C^2}\right)^{-1}$ *. Thus

$$(X_0, Y_0, Z_0) = \frac{eC^2\epsilon^{1/2}x}{(\epsilon x^2 + y^2 + z^2)^{3/2}}, \quad \frac{eC^2\epsilon^{-1/2}y}{(\epsilon x^2 + y^2 + z^2)^{3/2}}, \quad \frac{eC^2\epsilon^{-1/2}z}{(\epsilon x^2 + y^2 + z^2)^{3/2}}. \quad (1)$$

If we have a unit charge moving in company with the charge e , and with the same velocity, X_0, Y_0, Z_0 of course represents the force on it.

Suppose we consider the force on our moving unit when placed, not at the point x, y, z , but at the point $\epsilon^{-1/2}x, y, z$; its components X_1, Y_1, Z_1 are from (1)

$$(X_1, Y_1, Z_1) = \frac{eC^2x}{(x^2 + y^2 + z^2)^{3/2}}, \quad \frac{eC^2\epsilon^{-1/2}y}{(x^2 + y^2 + z^2)^{3/2}}, \quad \frac{eC^2\epsilon^{-1/2}z}{(x^2 + y^2 + z^2)^{3/2}}. \quad (2)$$

Now consider any electron a of our system at rest. Let e_1 be the strength of the electron. The component forces on it, due to an electron b of strength e_2 , whose x, y , and z components differ by x_1, y_1, z_1 , are P, Q, R , where

$$(P, Q, R) = \frac{e_1e_2C^2x_1}{(x_1^2 + y_1^2 + z_1^2)^{3/2}}, \quad \frac{e_1e_2C^2y_1}{(x_1^2 + y_1^2 + z_1^2)^{3/2}}, \quad \frac{e_1e_2C^2z_1}{(x_1^2 + y_1^2 + z_1^2)^{3/2}}.$$

Since a is in equilibrium, the x components due to the action of all the electrons on it, balance out, and a similar remark applies to the y and z components. If the system is set in motion, however, the components will not balance out in this way unless the system alters its dimensions, for the components due to each electron are altered by the motion to an extent which depends on the coordinates of that electron with respect to a . Suppose, however, that the matter shrinks in the x direction so that the x components of any pair of electrons are reduced in the ratio $\epsilon^{-1/2}$, then it follows from (2) that the x component forces on a due to the electron b , for example, are

$$\frac{e_1e_2C^2x_1}{(x_1^2 + y_1^2 + z_1^2)^{3/2}}, \quad \frac{e_1e_2C^2\epsilon^{-1/2}y_1}{(x_1^2 + y_1^2 + z_1^2)^{3/2}}, \quad \frac{e_1e_2C^2\epsilon^{-1/2}z_1}{(x_1^2 + y_1^2 + z_1^2)^{3/2}},$$

or

$$P, \quad \epsilon^{-1/2} Q, \quad \epsilon^{-1/2} R.$$

* 'Recent Researches in Electricity and Magnetism,' p. 17.

Thus all the x components on a are the same as before, so that if they balanced out before the motion, they will still balance out, and while the y components are not the same as when the system was at rest, they are all altered in the *same* ratio, so that if they balanced out before the motion was imparted, they will balance out when the body is moving, and a similar remark applies to the z components. Hence, the whole system will again be in equilibrium if it shrinks in this manner, and suitable constraints are applied at the boundary.

We must now pass on to the consideration of systems in which the electrons are in motion, even though the system as a whole is at rest. We may remark at once that the final state of such a system when set in motion with velocity v cannot be absolutely asserted without knowledge of the means by which that velocity is brought about; we know, as a matter of fact, that if we set a piece of lead, for example, in motion with a blow, the final condition of that lead will be different to what it would have been if it had gained its velocity gradually, the lead will be deformed by the blow, and though it may at first sight be thought that we are here introducing other considerations which ought not to be involved, we must I think admit them, for after all, our piece of lead is to be looked upon as simply an electromagnetic system, and on our present view, both the blow and the steady method of imparting the motion are means of producing the final velocity v , which, if our knowledge were sufficiently great, could be expressed completely as the result of certain external electromagnetic effects. The final state of the electronic motions is not, however, entirely dependent on the method of producing the velocity, the state is restricted by the final velocity v imparted, so that it is not unreasonable to suppose that if no sudden impulse is given to certain of the electrons, if all, so to speak, are acted on at once, the final state of motion of the electrons in the moving system will be sensibly independent of slight modifications in the method of producing the motion. If then we find a system in motion as a whole with velocity v , the relative motions of whose electrons are consistent with the electromagnetic laws, and which differ from those in the system at rest by amounts which get smaller and smaller, the smaller we make v , we may with a certain amount of confidence assert, that this is the system which the fixed system becomes when set in motion; this in fact is all that we can do without specific knowledge of the electronic motions, it is all that ever has been done, or can be done by any other method of considering the matter.

In what follows we shall look upon a piece of matter as simply a system of electrons in motion, and though we shall for convenience use the term "orbital motion," it will be seen that what is said is not restricted to the case where the electrons stay approximately in one place, and revolve round and near to fixed centres; it will apply even to cases where the electrons describe paths in which they wander from molecule to molecule. It is not even necessary to restrict our work to systems in equilibrium; indeed, the equilibrium of all electronic motions in a piece of matter is probably of a secular or possibly semi-statistical nature, there is at any rate always disintegration at the surface.

We shall then imagine a system of electrons S_1 , at rest as a whole, but having motions relative to one another which are consistent with the laws of electrodynamics. We shall then fix our attention on a corresponding system S_2 , moving in the direction of the axis of x with velocity v , and with the orbits of all its electrons shrunk in the direction of the axis of x in the ratio $\epsilon^{-1/2}$; we shall inquire whether movement of the electrons of S_2 can, consistently with the laws of electrodynamics, take place in these orbits, and if such motions are possible, we shall inquire how the nature of the motion in these orbits must be modified in order to make them possible. We shall find that such a type of motion is possible, and the necessary adjustment of the rates of motion in the orbits will bring out the real physical significance of the peculiar time variable occurring in Larmor's transformation.

First, with regard to the field produced by a moving electron. A moving mass of electricity, of volume density ρ , produces on unit charge at rest at a point P a force, each of whose components X, Y, Z consists of two parts, a part derivable from a potential ψ , and a part X_1, Y_1, Z_1 , arising out of the changing magnetic field at the point P. The potential ψ is of the form

$$\psi = C^2 \int \frac{1}{r} [\rho] dS$$

where dS is an element of volume, and the square bracket is meant to indicate that in considering the contribution of the element dS at the time t , we must not put in the value of ρ then existing in it, but the value which existed there at the time $t - \frac{r}{C}$, where r is the distance from the element to the point P. The components α, β, γ of the magnetic field may

also be made to depend on a vector potential A of the form

$$A = \int \frac{1}{r} [\rho W] dS$$

where the square brackets have the meaning assigned above, and W is the velocity of the electricity. If we like, we may interpret the above by saying, that an element of charge ρdS at rest at the point O produces at P a force derivable from a potential $\psi = \frac{C^2 \rho dS}{r}$, but when the charge is moving, and is at the point O , this part of the total force does not make its appearance until a time $\frac{r}{U}$ after the element has left O , this time of course representing the time taken for light to travel from O to P . An analogous remark applies to the expression for A . The magnetic field α, β, γ is related to the potential A in the manner expressed by

$$(\alpha, \beta, \gamma) = \left(\frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z}, \frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x}, \frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y} \right). \quad (3)$$

The force (X_1, Y_1, Z_1) is given by

$$(X_1, Y_1, Z_1) = - \left(\frac{\partial A_x}{\partial t}, \frac{\partial A_y}{\partial t}, \frac{\partial A_z}{\partial t} \right),$$

and the total force acting on an electron at rest in the æther, and of unit strength, is

$$(X, Y, Z) = \left(- \frac{\partial \psi}{\partial x} - \frac{\partial A_x}{\partial t}, - \frac{\partial \psi}{\partial y} - \frac{\partial A_y}{\partial t}, - \frac{\partial \psi}{\partial z} - \frac{\partial A_z}{\partial t} \right). \quad (4)$$

Thus the quantities ψ and A are all that are needed to completely determine the field. The values of ψ and A for a single point electron of strength e moving with velocity W are*

$$\psi = \frac{C^2 e}{\left[r \left(1 - \frac{W_r}{U} \right) \right]}, \quad A = \frac{e[W]}{\left[r \left(1 - \frac{W_r}{U} \right) \right]} \quad \cdot \quad \cdot \quad (5)$$

where r is the distance measured, not from the electron to the point P , but from some point O , previously occupied by the electron, and so situated that the time taken for the electron to pass from O to its present position is the same as the time taken for light to pass from O to P . W_r is the velocity of the electron resolved along the line OP .

* Lorentz, 'Theory of Electrons,' p. 50.

The whole field at the point P may be looked upon as being made up of the parts contributed by the individual electrons, the effect contributed by each electron depending on the position, and motion, suffered by that electron at a time δt earlier than t , where δt is a quantity varying for each electron, being in fact the time taken for light to travel from the point occupied by the electron at the time $t - \delta t$ to the point P. Thus to each instantaneous state of the æther at P, there corresponds a set of instantaneous electronic distributions and motions, which have occurred at varying times earlier than t , and which have been responsible for the state of affairs at P. We shall speak of these instantaneous motions as giving rise to a simultaneous set of forces at P, including of course in our meaning the whole field produced by the electrons, and not merely the part due to the motions alone.

Now in order to study the effect of uniform translatory motion on the force at P', the point in the moving system which corresponds to the point P in the fixed system*, we shall first find the condition, that if a certain set of instantaneous electronic motions give rise to a simultaneous set of forces at the point P in the fixed system, the corresponding set of instantaneous motions shall give rise to a simultaneous set of forces at the point P' in the moving system.

Consider two corresponding orbits of some electron in the fixed and moving systems respectively. Suppose that the time taken by the electron in the moving system to describe its orbit is k times the time taken by the electron in the fixed system, where k is a quantity as yet undetermined. In virtue of the different rates of description of the orbits, we shall periodically have our two electrons occupying corresponding points in their orbits at the same time, and as a matter of fact, choosing any point O in the orbit in the system at rest, we can always find some time sufficiently remote at which the electron in the fixed system occupied the point O and simultaneously the corresponding electron occupied the point O', which is the point in the moving system corresponding to O†. It will simplify matters if we take this remote instant as our origin of time. Now suppose that the instantaneous motion of our electron at the point O produces

* P' is the point to which P moves when the whole system S_1 is shrunk in the x direction in the ratio $\epsilon^{-1/2}$. It is in this sense that the word "Corresponding" is used.

† At least we can always find a time at which one electron occupied the point O and the other occupied a point which is as near to O' as we please.

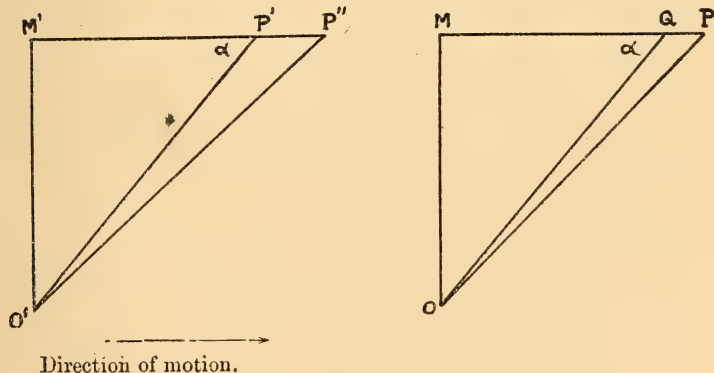
its effect at the point P in the system at rest at the time t ; the time at which that instantaneous motion must have occurred is obviously $t - \frac{OP}{C}$. The corresponding motion in the moving system will consequently be described at the time $k\left(t - \frac{OP}{C}\right)$ and the time at which this motion will give rise to its effect at the point P' in the moving system is

$$t' = k\left(t - \frac{OP}{C}\right) + \frac{O'P''}{C},$$

where O'P'' is the line joining O' in the moving system to the point P'' in space which will be occupied by the point P' when the effect due to the motion is felt at P'. Now it would be possible to find the condition which we seek, assuming any arbitrary value of k , but as we shall at a later stage of the paper find it necessary, for other reasons, to take k as $\epsilon^{1/2}$, we shall, to save unnecessary labour in the calculation, at once restrict ourselves to this case, and of course in doing this we are not making any assumption, we are simply restricting the conditions of the problem.

Now if P'M' (fig. 1) is the perpendicular on the zy plane

Fig. 1.



in the moving system, O' being taken as the origin, we have on writing

$$M'P' = \xi, \quad P'P'' = \delta\xi, \quad O'P' = r, \quad O'P'' = r_2,$$

the result

$$\frac{\delta\xi}{r_2} = \frac{v}{C}, \quad \dots \dots \dots (6)$$

for P' travels a distance $\delta\xi$ while the disturbance originating at O' travels O'P''.

Now

$$r_2^2 = r^2 + \delta\xi^2 + 2r \cdot \delta\xi \cos \alpha,$$

from which we obtain, on substituting for $\delta\xi$ the result given by (6), the expression

$$r_2 = \frac{r}{-\frac{v\xi}{Cr} + \left(\frac{\xi^2}{r^2} \cdot \frac{v^2}{C^2} + 1 - \frac{v^2}{C^2}\right)^{1/2}}.$$

Now consider the system at rest, and let M be the foot of the perpendicular from P on the zy plane. If we make MQ equal to ξ , we have, since $\frac{MP}{\xi} = \left(1 - \frac{v^2}{C^2}\right)^{-1/2}$,

$$PQ = \xi \left[\left(1 - \frac{v^2}{C^2}\right)^{-1/2} - 1 \right];$$

observing that the angle MQO is the same as the angle α in the figure for the moving system, we see that if we write $OP = r_1$,

$$r_1^2 = r^2 + \xi^2 \left[\left(1 - \frac{v^2}{C^2}\right)^{-1/2} - 1 \right]^2 + 2r\xi \left[\left(1 - \frac{v^2}{C^2}\right)^{-1/2} - 1 \right] \cos \alpha,$$

which reduces to

$$r_1 = \left[r^2 + \xi^2 \left(\frac{v^2}{C^2 - v^2} \right) \right]^{1/2}.$$

Thus, since $OP = r_1$ and $O'P'' = r_2$, our expression for t' becomes

$$t' = \left(t - \frac{OP}{C} \right) \epsilon^{1/2} + \frac{O'P''}{C} = t\epsilon^{1/2} + \frac{1}{C} \left[\frac{r}{-\frac{v\xi}{Cr} + \left(\frac{\xi^2}{r^2} \cdot \frac{v^2}{C^2} + 1 - \frac{v^2}{C^2}\right)^{1/2}} - \left(1 - \frac{v^2}{C^2}\right)^{-1/2} \left\{ r^2 + \xi^2 \left(\frac{v^2}{C^2 - v^2} \right) \right\} \right],$$

which after a little reduction reduces on writing x' for ξ to

$$t' = t\epsilon^{1/2} + \frac{\epsilon vx'}{C^2} \cdot \cdot \cdot \cdot \cdot \cdot (7)$$

Now write T_0 for the time at which the instantaneous motion considered occurs at O in the system at rest; the time at which the corresponding motion occurs at O' is $\epsilon^{1/2}T_0$, so that the time taken for the disturbance to be propagated to P'

from the electron in the moving system at O' is

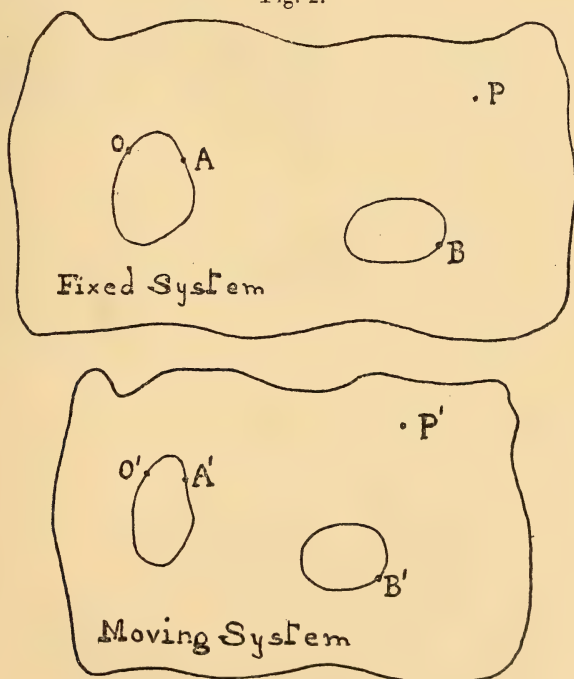
$$\delta T = \epsilon^{1/2}(t - T_0) + \frac{\epsilon v \alpha'}{C^2}.$$

It will be observed that this expression is independent of the origin of time which we choose; in fact, if we consider any instantaneous electronic motion in any orbit in the system at rest which occurs at the time T_1 and at the point A and which produces its effect at the point P at the time t , the interval between the occurrence of the corresponding motion and the production of the effect at the point P' in the moving system is

$$\delta T_1 = \epsilon^{1/2}(t - T_1) + \frac{\epsilon v \alpha'}{C^2}$$

where t and T_1 are measured from any origin, and α' is the difference of the x coordinates of P' and A'^* .

Fig. 2.



Now consider any two electrons e_1 and e_2 † which produce at the points A and B (fig. 2) in their respective orbits, and

* In all that follows, a dashed letter will refer to the moving system.

† The orbits shown in the figure are not intended necessarily to be in the same plane as the point P , nor indeed are they intended to be plane orbits at all, they may be of any shape.

at the times T_1 and T_2 , instantaneous motions which give rise to simultaneous effects at the point P at the time t , time being measured, to fix our ideas, from the instant when one of the electrons (say e_1) crossed some point O in its orbit in the system at rest, and at the same time the corresponding electron in the moving system passed the corresponding point O'. We then have in the moving system

Time taken by disturbance originated by e_1 to reach P'

$$= \delta T_1 = \epsilon^{1/2}(t - T_1) + \frac{\epsilon v \alpha'}{C^2}.$$

Time taken by disturbance originated by e_2 to reach P'

$$= \delta T_2 = \epsilon^{1/2}(t_1 - T_2) + \frac{\epsilon v}{C^2}(\alpha' - \beta'),$$

where α' and β' are the differences of the x coordinates of A' and P', and of A' and B' respectively, t_1 and T_2 being measured from the same origin as t and T . t_1 is of course the time of occurrence at P' of the disturbance produced by e_2 . If the disturbances due to e_1 and e_2 are to be simultaneous at the point P' in the moving system, we must have $t_1 = t$ and consequently

$$\delta T_1 - \delta T_2 = \epsilon^{1/2}(T_2 - T_1) + \frac{\epsilon v \beta'}{C^2}.$$

Since this is the amount by which the time for the passage of the disturbance originated by e_1 exceeds the time for the passage of the disturbance originated by e_2 , we see that the instantaneous motion of e_2 must, in the moving system, occur later than that of e_1 by $\epsilon^{1/2}(T_2 - T_1) + \frac{\epsilon v \beta'}{C^2}$. This condition is satisfied if the motion at A' occurs at the time $\epsilon^{1/2}T_1 + \frac{\epsilon v x_1'}{C^2}$

and the motion at B' at the time $\epsilon^{1/2}T_2 + \frac{\epsilon v x_2'}{C^2}$, where x_1' and x_2' are the coordinates of A' and B' measured from any origin we choose. Thus we may say that if a series of electronic motions occur at the points $x_1, y_1, z_1, x_2, y_2, z_2, x_3, y_3, z_3$, &c. at the times T_1, T_2, T_3 , &c. in the system at rest, and give rise to a simultaneous set of effects at some point P, the condition that the corresponding motions occurring at the corresponding points $x_1', y_1, z_1, x_2', y_2, z_2$, &c. shall give rise to simultaneous effects at P' in the moving system is, that they shall occur at times $\epsilon^{1/2}T_1 + \frac{\epsilon v x_1'}{C^2}$, $\epsilon^{1/2}T_2 + \frac{\epsilon v x_2'}{C^2}$... &c., which is equivalent to saying that if T is

the time of occurrence of any electronic motion at x, y, z in the system at rest, the necessary requirements are satisfied if the corresponding electronic motion occurs in the moving

system at the point x', y, z , at the time $\epsilon^{1/2}T + \frac{\epsilon v x'}{C^2}$. Now

we have already seen that if an electronic motion occurring at O produces its effect at the point P at the time t in the system at rest, the effect due to the corresponding motion at

O' will occur at P' at the time $t' = \epsilon^{1/2}t + \frac{\epsilon v x'}{C^2}$. We are not

yet at liberty to say that, measuring time from the same

origin, if an electronic motion occurring at the point A produces its effect at P at the time t_a , the corresponding electronic motion occurring at A' will produce its effect at the

time $\epsilon^{1/2}t_a + \frac{\epsilon v x'}{C^2}$. We can readily see that this is so, how-

ever, for let us take O and O' as our origins of coordinates in the two systems, suppose the motion at A to take place at time T_a and suppose the effect to be felt at P at the time t_a . Then,

as we have already seen, if x' is the x coordinate of P' and

β' that of A', the motion occurs at A' at the time $\epsilon^{1/2}T_a + \frac{\epsilon v \beta'}{C^2}$,

and the disturbance produced by it at P' occurs later than

the motion at A' by an amount $\epsilon^{1/2}(t_a - T_a) + \frac{\epsilon v}{C^2}(x' - \beta')$.

Hence the disturbance at P' occurs at the time

$$\left[\epsilon^{1/2}T_a + \frac{\epsilon v \beta'}{C^2} \right] + \left[\epsilon^{1/2}(t_a - T_a) + \frac{\epsilon v}{C^2}(x' - \beta') \right] = \epsilon^{1/2}t_a + \frac{\epsilon v x'}{C^2}.$$

Thus we see that the requirement stated on page 70 is satisfied provided that, if any electron in the system at rest describes an instantaneous motion at the point ξ, η, ζ at the time T, the corresponding electron in the system in motion shall describe its corresponding instantaneous motion at the corre-

sponding point ξ', η, ζ , at the time $\epsilon^{1/2}T + \frac{\epsilon v \xi'}{C^2}$; and we have

further shown, that if the effect of a certain set of instantaneous motions is felt simultaneously at the time t at any point x, y, z in the system at rest, the effect due to the corresponding motions in the moving system will be felt at

the corresponding point x', y, z at the time $t' = \epsilon^{1/2}t + \frac{\epsilon v x'}{C^2}$.

The origins of the spacial coordinates in the above are,

strictly speaking, to be chosen as any corresponding points in the two systems which at some instant in the whole range of time are occupied simultaneously by corresponding electrons, and the origin of time may be taken as any time at which this occurs. As a matter of fact, the *origin* of time does not concern us; all we are concerned with is difference of time, and we may obviously measure our spacial coordinates in the two systems from any *corresponding* origins we choose, for differences in the choice of the spacial origin only obviously affect the expressions for the above times by a constant.

The above result is, of course, equivalent to the statement that the condition which must hold is, that if x', y', z' are the coordinates of any electron in the moving system,

$\epsilon^{1/2}x', y', z'$ must be the same functions of $\epsilon^{-1/2}t - \epsilon^{1/2}\frac{vx'}{C^2}$ as

the x, y, z coordinates in the fixed system are functions of t , and we further see that the values of $\epsilon^{1/2}x', y', z'$ for which any state of the æther (due to a certain set of electronic motions) occurs in the system in motion, are the same func-

tions of $\epsilon^{-1/2}t - \epsilon^{1/2}\frac{vx'}{C^2}$ as the values of x, y, z for the state of

the æther in the system at rest (due to the corresponding motions there), are functions of t .

It is interesting to observe that no electromagnetic phenomena have been involved in the deduction of the above facts with regard to the time variable, we have simply used the word "electron" to fix our ideas. The only fundamental thing involved is the idea of the finite time of propagation of an effect from a moving centre of disturbance.

We must now pass on to consider how the forces due to the electronic motions are modified by the motion of the system as a whole. On page 69 we have written down the forces X, Y, Z on a fixed unit of charge at a point P due to a moving electron a of strength e . If the unit at P is itself moving with velocity p_1, q_1, r_1 it constitutes a current in a magnetic field, so that owing to this fact there will be an additional force on it whose components are $q_1\gamma - r_1\beta, r_1\alpha - p_1\gamma, p_1\beta - q_1\alpha$. Thus the total force on our moving unit will be X_2, Y_2, Z_2 , where

$$\begin{aligned} (X_2, Y_2, Z_2) = & (X + q_1\gamma - r_1\beta, \quad Y + r_1\alpha - p_1\gamma, \\ & Z + p_1\beta - q_1\alpha) \quad . \quad . \quad . \quad (8) \end{aligned}$$

Now let us impart to the whole system a velocity v in the direction of the x axis. Let us suppose the electrons to be

constrained to move in the manner required by the investigation on pages 70-76, and let us see whether the modifications of the forces of the various electrons on one another is such as to maintain that state of motion. First let us see how the component velocities of an electron, whose component velocities in the system at rest are denoted by p, q, r , will be modified by the motion.

Suppose that the x coordinate of a , in the system at rest, is some function of the time, say $x=f(t)$ so that

$$\frac{dx}{dt} = f'(t) = p.$$

Then in the moving system we have

$$\epsilon^{1/2}x' = f\left(\epsilon^{-1/2}t - \epsilon^{1/2}\frac{vx'}{C^2}\right),$$

$$\therefore \epsilon^{1/2}\frac{dx'}{dt} = \left[f'\left(\epsilon^{-1/2}t - \epsilon^{1/2}\frac{vx'}{C^2}\right)\right]\left[\epsilon^{-1/2} - \epsilon^{1/2}\frac{v}{C^2}\frac{dx'}{dt}\right],$$

or, replacing t by $\epsilon^{1/2}t + \frac{\epsilon vx'}{C^2}$, in order to find the value of $\frac{dx'}{dt}$ when the electron is describing the motion corresponding to the one we are considering in the fixed system, we find

$$\frac{dx'}{dt} = p\epsilon^{-1}\left(1 + \frac{vp}{C^2}\right)^{-1},$$

so that the velocity p' with respect to a fixed origin is

$$p' = v + p\epsilon^{-1}\left(1 + \frac{vp}{C^2}\right)^{-1}.$$

In a similar manner we obtain

$$q' = q\epsilon^{-1/2}\left(1 + \frac{vp}{C^2}\right)^{-1},$$

$$r' = r\epsilon^{-1/2}\left(1 + \frac{vp}{C^2}\right)^{-1}.$$

. . . (9)

Now let us consider the values of ψ and ψ' at corresponding points in the fixed and moving systems respectively. Returning to fig. 1 we remember that OP represents the distance from some point O in the system at rest, at which an electronic motion took place, to the point P at which the effect was felt at the time t , while O'P'' represents the distance from the point O' to P'', which is the point in space

to which the point P' has moved by the time that the effect due to the electronic motion at O' is felt there. Thus writing

$$OP = S \quad \text{and} \quad O'P'' = S_2$$

we have, for the values of ψ and ψ' at corresponding points and times

$$\psi = \frac{C^2 e}{\left[S \left(1 - \frac{W_s}{C} \right) \right]}, \quad \psi' = \frac{C^2 e}{\left[S_2 \left(1 - \frac{W_{s_2}'}{C} \right) \right]},$$

where W_s and W_{s_2}' are the values of the velocities of the corresponding electrons in the two systems, resolved along OP and $O'P''$ respectively. Since, as we have seen on page 72,

$$\left(t - \frac{OP}{C} \right) \epsilon^{1/2} + \frac{O'P''}{C} = t \epsilon^{1/2} + \frac{\epsilon v x'}{C^2},$$

and since $\frac{\epsilon^{1/2} x'}{S} \cdot v$ is v_s , i. e. the velocity of the system resolved along OP , we have

$$S_2 = S \epsilon^{1/2} \left(1 + \frac{v_s}{C} \right).$$

Now if l, m, n and l', m', n' are the direction cosines of the lines OP and $O'P''$ respectively, we have, using the notation of page 71, and remembering that $\delta \xi = \frac{v S_2}{C}$,

$$l' = (\xi + \delta \xi) S_2^{-1} = \epsilon^{1/2} \xi S^{-1} \epsilon^{-1} \left(1 + \frac{v_s}{C} \right)^{-1} + \frac{v}{C},$$

$$\text{i. e., } l' = l \epsilon^{-1} \left(1 + \frac{v_s}{C} \right)^{-1} + \frac{v}{C} = \left(l + \frac{v}{C} \right) \left(1 + \frac{v_s}{C} \right)^{-1};$$

also we see at once that

$$(m', n') = m \epsilon^{-1/2} \left(1 + \frac{v_s}{C} \right)^{-1}, \quad n \epsilon^{-1/2} \left(1 + \frac{v_s}{C} \right)^{-1}.$$

Observing that

$$W_{s_2}' = l' p' + m' q' + n' r',$$

we have

$$S_2 \left(1 - \frac{W_{s_2}'}{C} \right) = S \epsilon^{1/2} \left(1 + \frac{v_s}{C} \right) \left(1 - \frac{l' p' + m' q' + n' r'}{C} \right).$$

Putting in the values of p' , q' , r' given by (9), and the values of l' , m' , n' given above, and remembering that

$$\epsilon^{-1} = 1 - \frac{v^2}{C^2}, \quad \text{and} \quad lv = v_s,$$

we readily obtain

$$S_2 \left(1 - \frac{W_{s_2}'}{C} \right) = \epsilon^{-1/2} S \left(1 - \frac{W_s}{C} \right) \left(1 + \frac{vp}{C^2} \right)^{-1}.$$

Now this is the quantity which, in the moving system, replaces $S \left(1 - \frac{W_s}{C} \right)$ in the expression for ψ in the fixed system, so that since, as is readily seen from (5),

$A_x = \frac{p}{C^2} \psi$; we have, at corresponding points and times,

$$\psi' = \epsilon^{1/2} \psi + \epsilon^{1/2} v A_x.$$

Again, making use of the relation (5) and substituting the values of p' , q' , r' , in terms of p , q , r , we have, at corresponding points and times,

$$(A_x', A_y', A_z') = \frac{e(v+p)}{\epsilon^{-1/2} \left[S \left(1 - \frac{W_s}{C} \right) \right]}, \quad \frac{e\epsilon^{-1/2}q}{\epsilon^{-1/2} \left[S \left(1 - \frac{W_s}{C} \right) \right]},$$

$$\frac{e\epsilon^{-1/2}r}{\epsilon^{-1/2} \left[S \left(1 - \frac{W_s}{C} \right) \right]},$$

or

$$A_x', A_y', A_z' = \epsilon^{1/2} \left(\frac{v}{C^2} \psi + A_x \right), A_y, A_z.$$

Writing

$$(x'', y'', z'', t'') = \left(\epsilon^{1/2} x', y', z', \epsilon^{-1/2} t - \epsilon^{1/2} \frac{vx'}{C^2} \right),$$

we see that the above is equivalent to the statement that ψ' , A_x' , A_y' , A_z' are the same functions of x'' , y'' , z'' and t'' in the moving system, as in the fixed system,

$$\epsilon^{1/2} (\psi + v A_x), \quad \epsilon^{1/2} \left(\frac{v}{C^2} \psi + A_x \right), \quad A_y, \quad A_z$$

are functions of x , y , z , and t . Since $x' = x - vt$, we have

$$\left. \begin{aligned} \frac{\partial}{\partial x} &= \epsilon^{1/2} \frac{\partial}{\partial x''} - \epsilon^{1/2} \frac{v}{C^2} \frac{\partial}{\partial t''}, & \frac{\partial}{\partial t} &= \epsilon^{1/2} v \frac{\partial}{\partial t''} - \epsilon^{1/2} \frac{v}{C^2} \frac{\partial}{\partial x''}, \\ \left(\frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) &= \left(\frac{\partial}{\partial y''}, \frac{\partial}{\partial z''} \right), \end{aligned} \right\} \quad (10)$$

80 Dr. W. F. G. Swann on the *Effects of Uniform Motion*
so that at corresponding points and times

$$\left. \begin{aligned} \frac{\partial \psi'}{\partial x} &= \epsilon \frac{\partial \psi}{\partial x} - \frac{\epsilon v}{U^2} \frac{\partial \psi}{\partial t} + \epsilon v \frac{\partial A_x}{\partial x} - \frac{\epsilon v^2}{U^2} \frac{\partial A_x}{\partial t}, \\ \frac{\partial \psi'}{\partial y} &= \epsilon^{1/2} \left(\frac{\partial \psi}{\partial y} + v \frac{\partial A_x}{\partial y} \right), \quad \frac{\partial \psi'}{\partial z} = \epsilon^{1/2} \left(\frac{\partial \psi}{\partial z} + v \frac{\partial A_x}{\partial z} \right), \\ \frac{\partial A_x'}{\partial t} &= \frac{\epsilon v}{U^2} \frac{\partial \psi}{\partial t} + \epsilon \frac{\partial A_x}{\partial t} - \frac{\epsilon v^2}{U^2} \frac{\partial \psi}{\partial x} - \epsilon v \frac{\partial A_x}{\partial x}, \\ \frac{\partial A_y'}{\partial t} &= \epsilon^{1/2} \left(\frac{\partial A_y}{\partial t} - v \frac{\partial A_y}{\partial x} \right), \quad \frac{\partial A_z'}{\partial t} = \epsilon^{1/2} \left(\frac{\partial A_z}{\partial t} - v \frac{\partial A_z}{\partial x} \right). \end{aligned} \right\} (11)$$

Making use of equations (4) and also of equations (3) for the magnetic vector, we obtain, on substituting the values of $\frac{\partial \psi'}{\partial x} \dots$ &c. from (11),

$$\left. \begin{aligned} X' &= -\frac{\partial \psi}{\partial x} - \frac{\partial A_x}{\partial t} = X, \\ Y' &= -\epsilon^{1/2} \left(\frac{\partial \psi}{\partial y} + \frac{\partial A_y}{\partial t} \right) + \epsilon^{1/2} v \left(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y} \right) = \epsilon^{1/2} (Y + v\gamma), \\ Z' &= -\epsilon^{1/2} \left(\frac{\partial \psi}{\partial z} + \frac{\partial A_z}{\partial t} \right) - \epsilon^{1/2} v \left(\frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x} \right) = \epsilon^{1/2} (Z - v\beta). \end{aligned} \right\} (12)$$

By an exactly similar process, on making use of the expressions for the magnetic vector, and substituting the values of the spacial derivatives of A_x', A_y', A_z' in terms of the derivatives at the corresponding point and time in the fixed system, we obtain

$$\left. \begin{aligned} \alpha' &= \alpha, \\ \beta' &= \epsilon^{1/2} \left(\beta - \frac{v}{U^2} Z \right), \\ \gamma' &= \epsilon^{1/2} \left(\gamma + \frac{v}{U^2} Y \right), \end{aligned} \right\} \dots \dots \dots (13)$$

By a mere algebraical combination of (12) and (13) it follows that, at corresponding points and times,

$$\left. \begin{aligned} \epsilon^{1/2} (\epsilon^{-1/2} \alpha', \beta' + \frac{v}{U^2} Z', \gamma' - \frac{v}{U^2} Y', \epsilon^{-1/2} X', Y' - v\gamma', Z' + v\beta') \\ = (\alpha, \beta, \gamma, X, Y, Z). \end{aligned} \right\} (14)$$

Again, if X_2, Y_2, Z_2 and X_2', Y_2', Z_2' are the component forces due to the electron a on the unit electron b in the fixed and moving systems respectively, and if p_1, q_1, r_1 and p_1', q_1', r_1' are the corresponding component velocities of b in the two systems, we see from equations (8) that

$$(X_2', Y_2', Z_2') = X' + q_1'\gamma' - r_1'\beta', \quad Y' + r_1'\alpha' - p_1'\gamma', \\ Z' + p_1'\beta' - q_1'\alpha'.$$

Using the values of p_1', q_1', r_1' in terms of p_1, q_1, r_1 as given by (9) and the values of $X', Y', Z', \alpha', \beta', \gamma'$ given by (12) and (13), we find that it is only by neglect of quantities of the order $\frac{W}{v} \left(\frac{v^2}{C^2} \right)$ that we can express the force at a point in the moving system in terms of the force at the corresponding point in the fixed system, without explicitly introducing the velocities of the electrons relative to the system as a whole. We shall discuss this restriction on page 85, but accepting it for the present, we find that at corresponding points and times

$$(X_2', Y_2', Z_2') = X + q_1\gamma - r_1\beta, \quad \epsilon^{-1/2}(Y + r_1\alpha - p_1\gamma). \\ \epsilon^{-1/2}(Z + p_1\beta - q_1\alpha),$$

or
$$(X_2', Y_2', Z_2') = (X_2, \epsilon^{-1/2}Y_2, \epsilon^{-1/2}Z_2).$$

In view of the fact that if a set of instantaneous electronic motions in the system at rest give rise to simultaneous effects at a point, the corresponding motions give rise to simultaneous effects at the corresponding point and time in the moving system, we may extend what has been proved above for the vectors due to the motion of a single electron, to the total values of the vectors due to the motions of all the electrons. Thus, if P, Q, R and P', Q', R' represent the component forces on a unit electron in the fixed and moving systems respectively, we have at corresponding points and times

$$(P', Q', R') = (P, \epsilon^{-1/2}Q, \epsilon^{-1/2}R),$$

which is, of course, equivalent to the statement that $P', \epsilon^{1/2}Q', \epsilon^{1/2}R'$ must be the same functions of

$$\epsilon^{1/2}x', y', z', \quad \text{and} \quad \epsilon^{-1/2}t - \epsilon^{1/2} \frac{vx'}{C^2}$$

in the moving system, as in the fixed system P, Q, R are
Phil. Mag. S. 6. Vol. 23. No. 133. Jan. 1912. G

functions of x, y, z , and t . We may also here remark that, since

$$4\pi C^2(f, g, h) = (X, Y, Z),$$

the results deduced in equation (14) are equivalent to the statement that

$$\left. \begin{aligned} \epsilon^{1/2} \left(\epsilon^{-1/2} \alpha', \beta' + 4\pi v h', \gamma' - 4\pi v g', \epsilon^{-1/2} f', g' - \frac{v}{4\pi C^2} \gamma', h' + \frac{v}{4\pi C^2} \beta' \right) \\ \text{are the same functions of} \\ \epsilon^{1/2} x', y', z' \quad \text{and} \quad \epsilon^{-1/2} t - \epsilon^{1/2} \frac{v x'}{C^2} \end{aligned} \right\} \quad (15)$$

in the moving system, as in the fixed system ($\alpha, \beta, \gamma, f, g, h$) are functions of x, y, z , and t ; for, as we have above remarked, the results obtained for the vectors due to a single electron may be extended to the total vectors due to all the electrons. The above results are, of course, the same as those obtained by Larmor's transformation. Let us now see whether the modifications of the forces on the electrons, produced by the motion, are such as to maintain them in the state of orbital motion which we have assigned to them.

The measure of the force acting on the electron in any direction is the rate of increase of the total momentum associated with the electron in that direction. In order to find the accelerations λ, μ, ν , produced on our electron b by unit component forces in the three coordinate directions, we have to find by how much the velocity must increase in each of those directions, in order that the momentum associated with the motion in the particular direction considered may increase by unity, so that if U, V, W are the component momenta in the three coordinate directions, expressed as functions of the coordinate velocities p_1, q_1, r_1 , the component accelerations satisfy three equations of the typical form

$$1 = \frac{dU}{dt} = \lambda \frac{\partial U}{\partial p_1} + \mu \frac{\partial U}{\partial q_1} + \nu \frac{\partial U}{\partial r_1} \dots \quad (16)$$

The most important case is where the electron is moving parallel to the x axis with velocity v , so that $p_1 = v, q_1 = r_1 = 0$. I have, in a former communication*, calculated the values of λ, μ, ν for this case, assuming, after Lorentz, that the electron, like the matter as a whole, contracts when in

* Phil. Mag. June 1911, p. 733, also July 1911, p. 223.

motion in the ratio $\epsilon^{-1/2}$ *, and it will be unnecessary to repeat the work here. The quantities λ^{-1} , μ^{-1} , ν^{-1} for this case are, of course, the so-called longitudinal and transverse masses of the electron, first deduced by J. J. Thomson, by Lorentz, and by Abraham, by another method. It is easily seen, from the work in my paper above mentioned, that to the degree of approximation to which we have restricted ourselves on page 81, the expressions for λ , μ , ν given by equations (16) are the same as those for the cases $p_1=v$, $q_1=r_1=0$, and these turn out to be

$$\lambda = n_0 \epsilon^{-3/2}, \quad \mu = n_0 \epsilon^{-1/2}, \quad \nu = n_0 \epsilon^{-1/2},$$

where n_0 is the acceleration produced by unit force on the electron in the system at rest, which, to the degree of approximation referred to on page 81, is constant, and independent of the direction of the force.

Suppose now that the component forces on our electron b in the system at rest are functions of x , y , z , and t of the forms

$$P = F_1(x, y, z, t), \quad Q = F_2(x, y, z, t), \quad R = F_3(x, y, z, t),$$

then, as we have seen on page 81, the forces P' , Q' , R' in the moving system are given by

$$\begin{aligned} P' &= F_1(\epsilon^{1/2}x', y', z', t''), & \epsilon^{1/2}Q' &= F_2(\epsilon^{1/2}x', y', z', t''), \\ & & \epsilon^{1/2}R' &= F_3(\epsilon^{1/2}x', y', z', t''), \end{aligned}$$

$$\text{where} \quad t'' = \epsilon^{-1/2}t - \epsilon^{1/2} \frac{vx'}{C^2}.$$

The equations of motion of our electron, in the fixed system, are

$$\left. \begin{aligned} \frac{d^2x}{dt^2} &= n_0 F_1(x, y, z, t), & \frac{d^2y}{dt^2} &= n_0 F_2(x, y, z, t), \\ & & \frac{d^2z}{dt^2} &= n_0 F_3(x, y, z, t). \end{aligned} \right\} \quad \cdot \quad \cdot \quad (17)$$

and those of the corresponding electron in the moving

* In considering the force due to an electron at a distance large compared with its dimensions, the shape of the electron is not involved, but in considering the effect of the forces of the field *on* an electron, the shape is of vital importance, for no matter how small the electron may be, its effective mass depends on its shape, since practically the whole of the electrokinetic momentum associated with it is contained within a region of the same order of magnitude as itself.

system are, in view of the alteration of the accelerations produced by unit forces on the electron,

$$\left. \begin{aligned} \frac{d^2 x'}{dt^2} &= n_0 \epsilon^{-3/2} F_1(\epsilon^{1/2} x', y', z', t'')^*, \\ \frac{d^2 y'}{dt^2} &= n_0 \epsilon^{-1/2} \epsilon^{-1/2} F_2(\epsilon^{1/2} x', y', z', t''), \\ \frac{d^2 z'}{dt^2} &= n_0 \epsilon^{-1/2} \epsilon^{-1/2} F_3(\epsilon^{1/2} x', y', z', t''). \end{aligned} \right\} \quad (18)$$

Now the orbit of the electron in the system at rest is the curve of intersection of two surfaces,

$$\phi(x, y, z) = 0, \quad \text{and} \quad \chi(x, y, z) = 0,$$

which are obtained by eliminating t from equations (17). The question is, shall we on eliminating t from equations (18) obtain two surfaces of the form

$$\phi(\epsilon^{1/2} x', y', z') = 0, \quad \text{and} \quad \chi(\epsilon^{1/2} x', y', z') = 0?$$

Now observing that

$$\frac{d}{dt} = \frac{dt''}{dt} \cdot \frac{d}{dt''} = \left(\epsilon^{-1/2} - \frac{v}{C^2} \frac{dx'}{dt} \right) \frac{d}{dt''} = \epsilon^{-1/2} \frac{d}{dt''} - \frac{v^2}{C^2} \left(\frac{1}{v} \frac{dx'}{dt} \right) \frac{d}{dt''},$$

we see that, neglecting the second term of the last expression, which we are entitled to do, to the degree of approximation to which we are working, we can write $\frac{d}{dt}$ as $\epsilon^{-1/2} \frac{d}{dt''}$, and our equations (18) take the form

$$\left. \begin{aligned} \frac{d^2(\epsilon^{1/2} x')}{dt''^2} &= n_0 F_1(\epsilon^{1/2} x', y', z', t''), \\ \frac{d^2 y'}{dt''^2} &= n_0 F_2(\epsilon^{1/2} x', y', z', t''), \\ \frac{d^2 z'}{dt''^2} &= n_0 F_3(\epsilon^{1/2} x', y', z', t''); \end{aligned} \right\} \quad (19)$$

from which it is obvious, that if

$$\phi(x, y, z) = 0 \quad \text{and} \quad \chi(x, y, z) = 0$$

are the surfaces obtained by eliminating t from (17), then

$$\phi(\epsilon^{1/2} x', y', z') = 0 \quad \text{and} \quad \chi(\epsilon^{1/2} x', y', z') = 0$$

are the surfaces obtained by eliminating t'' , and consequently

* Strictly, we should write $\frac{d^2 x}{dt^2}$ where $x = x' + vt$. Since v is constant, however, $\frac{d^2 x}{dt^2} = \frac{d^2 x'}{dt'^2}$.

t , from equations (19). The intersection of these surfaces gives, of course, the contracted orbit which we expected, and our investigation consequently shows us, that if the electrons in the moving system move in the contracted orbits we have assumed, and in the manner determined by the investigation on pages 70-76, their mutual forces on one another, brought about by these motions, are such as to keep them moving in those orbits, without any external forces being applied.

The above investigation has involved the neglect of quantities of the order $\frac{W}{v} \left(\frac{v^2}{C^2} \right)$, where W is the velocity of an electron relative to the system as a whole ; thus the results are only true to the second order of $\frac{v}{C}$ provided that $\frac{W}{v}$ may be considered as a first order quantity, a result not likely to be true in practice. The investigation is, however, true to any order of $\frac{v}{C}$, provided that W is sufficiently small. It may be argued that, in limiting the investigation to small values of W we are practically restricting ourselves to a system in which there are no orbital motions, and that consequently we achieve no more by our work than has been achieved by the investigations on pages 66 and 67, for a case in which the electrons in the system at rest are absolutely devoid of motion ; the point is, however, that directly we allow any finite value to the orbital motions, however small, we are able to conceive our system as being one in secular equilibrium, and though no system with such small orbital velocities may actually be found in practice, we may look upon this system as one ideally possible. At first sight a difficulty suggests itself, owing to the fact that the smaller the value of v , the larger the value of $\frac{W}{v}$ and apparently the more inexact our analysis, but we must realize that as v is made smaller and smaller, the whole effect of the translatory motion becomes more and more inappreciable, and our analysis is always true to the order $\frac{Wv}{C^2}$.

As has been remarked on page 81, if quantities of the order of $\left(\frac{W}{v} \right) \left(\frac{v^2}{C^2} \right)$ are not negligible, the orbital velocities of the individual electrons will make their appearance explicitly in our expressions for the effects of imparting the translatory

motion, which would mean that the effects produced by that motion would depend on the elastic properties of the material, which of course, on our present view, are entirely determined by the nature of the electronic motions. As a matter of fact, this is really what might be expected to be the case, were it not for the fact that no matter what material is used in the apparatus, no experiment so far devised to detect an effect due to the earth's motion through space has given a positive result, which drives us to the somewhat unsatisfactory conclusion that, on the electron theory of matter, though the orbital velocities are almost certainly not small, the motions in any molecule probably combine together to produce, at external points, the equivalent of slow orbital motions, somewhat after the analogy of beats in sound. It would, I think, be interesting if the Michelson and Morley experiment could be repeated with the body of the apparatus made of some strongly magnetic material, such as iron, for we know that in such a material the orbital motions are capable of making themselves very evident.

It may be remarked, that since expressions (15) are exactly true however large W or v may be, the equilibrium of the moving system studied follows absolutely when the electrons are considered simply as singularities moving in accordance with the electromagnetic scheme. This apparent avoidance of the difficulty is illusory, however (as I propose to show in the communication following), owing to the fact that in this method of treatment it is vitally essential to consider the whole transition from the fixed to the moving state of the system.

University of Sheffield,
April 28th, 1911.

VI. *The Fitz Gerald Lorentz Contraction, and an Examination of the Method of Determining the Motions of Electrons, when considered simply as Singularities, moving so as to satisfy the Electromagnetic Scheme. By W. F. G. SWANN, D.Sc., A.R.C.S., Assistant Lecturer in Physics at the University of Sheffield*.*

IN his 'Æther and Matter,' Sir Joseph Larmor develops the consequences of the view that matter is an assemblage of electrons, in secular equilibrium under the influence of their mutual fields. In considering the laws which must determine the motions of the electrons, he points out that all idea of forces must be abolished, and the problem must be

* Communicated by the Author.

formulated "as that of the determination of the natural sequence of changes in the configuration of the system." In § 51, and in Chapter x. of 'Æther and Matter,' the general outline of the method is sketched. The essential point is, that a complete basis for the explanation of all the phenomena involved is to be found in the electromagnetic equations, which give the time rates of change of the ætherial displacement f, g, h , and the magnetic induction a, b, c , in equations of the type

$$4\pi \frac{\partial f}{\partial t} = \frac{\partial c}{\partial y} - \frac{\partial b}{\partial z}, \quad -(4\pi C^2)^{-1} \frac{\partial a}{\partial t} = \frac{\partial h}{\partial y} - \frac{\partial g}{\partial z} \quad (1)$$

where C is the velocity of light.

The electron is a singular point in the æther, near which the ætherial displacement increases indefinitely. The past, present, and subsequent history of the electrons in a piece of matter, and indeed of the whole universe, are completely determined when we have f, g, h and a, b, c given as functions of x, y, z and t , satisfying the electromagnetic equations; indeed, it is sufficient to know the values of f, g, h , and of the special derivatives of f, g, h, a, b, c , at one instant, to determine the whole history of the system. The equations implicitly involve the condition that, if

$$\frac{\partial f}{\partial x} + \frac{\partial g}{\partial y} + \frac{\partial h}{\partial z}$$

is zero at any point and time, it shall be for ever zero at that point, so that it is necessary to postulate that the equations need not hold at a singularity, as otherwise we should restrict our electrons to remain permanently at rest. The electrons are then the places where

$$\frac{\partial f}{\partial x} + \frac{\partial g}{\partial y} + \frac{\partial h}{\partial z}$$

is not zero, this being in fact the analytical criterion for finding their motions.

As an example, suppose that we were given f, g, h, a, b, c , as functions of the form

$$4\pi(f, g, h) = \frac{C^2 e \epsilon^{1/2}}{[\epsilon(x-vt)^2 + y^2 + z^2]^{3/2}} \left\{ (x-vt), y, z, \right\}$$

$$(a, b, c) = \frac{C^2 e \epsilon^{1/2}}{[\epsilon(x-vt)^2 + y^2 + z^2]^{3/2}} \left\{ 0, -vz, vy, \right\}$$

where $\epsilon^{-1} = 1 - \frac{v^2}{C^2}$.

We know that these represent the field of an electron of strength e , moving along the axis of x with velocity v . Suppose, however, that we did not know this; we should find by direct differentiation that these functions satisfied (1), and we should find that

$$\frac{\partial f}{\partial x} + \frac{\partial g}{\partial y} + \frac{\partial h}{\partial z}$$

was zero at all points in space, except where the relation $x=vt$, $y=z=0$ held, in which case it would become infinite, telling us that there was an electron moving along the axis of x with velocity v^* . It is easy to see how the same line of argument applies to more complicated systems. By transforming the electromagnetic equations to moving axes, Sir Joseph Larmor shows ('Æther and Matter,' Chapter xi.), that if $f_1, g_1, h_1, a_1, b_1, c_1$, expressed as functions of x_1, y_1, z_1, t_1 , represent the spontaneous changes of an electromagnetic system S referred to axes at rest in the æther, the same functions of

$$\epsilon^{1/2}x', y', z', \quad \epsilon^{-1/2}t - \epsilon^{1/2}\frac{vx'}{C^2},$$

will represent

$$\epsilon^{1/2}\left(\epsilon^{-1/2}f, g - \frac{v}{4\pi C^2}c, h + \frac{v}{4\pi C^2}b, \epsilon^{-1/2}a, b + 4\pi v h, c - 4\pi v g\right),$$

where f, g, h, a, b, c are the ætherial displacement and magnetic vectors for another electromagnetic system S_1 , and x', y', z', t' are referred to axes moving in the x direction with velocity v . By an electromagnetic system, we mean a system which satisfies the electromagnetic scheme at all points in space, except at the singularities.

If corresponding points and times in the two systems above are related by the equations

$$(x_1, y_1, z_1) = (\epsilon^{1/2}x', y', z'), \quad t_1 = \epsilon^{-1/2}t' - \epsilon^{1/2}v\frac{x'}{C^2},$$

the absolute correspondence of the singularities in the two

* It seems to me, that it is easier to take the condition f, g , or h equal to infinity as the criterion for the determination of the position of a singularity, rather than the condition that $\frac{\partial f}{\partial x} + \frac{\partial g}{\partial y} + \frac{\partial h}{\partial z}$ shall not be zero, for f, g, h must each become infinite at a singularity, and they cannot become infinite elsewhere. The criterion $f=\infty$ immediately leads to the determination of the motion of the singularity in the example quoted above, and moreover it immediately leads to the absolute correspondence of the singularities in the two systems S and S_1 , to any order of v/C .

systems follows to any order of $\frac{v}{C}$, the restriction to the second order involved in 'Æther and Matter' being now generally known to be unnecessary. Corresponding singularities in the two systems are shown to be of the same strengths, and it is concluded that the system S_1 represents what S becomes when set in motion; the theorem thus indicates a contraction of the system in the ratio $\epsilon^{-1/2}$ to unity.

The present paper forms an inquiry as to how far the above conclusion is justified, and in fact, as to how far the electromagnetic equations, by themselves, do form a sufficient basis for the explanation of all the phenomena concerned. The points involved are perhaps best introduced by considering one or two actual examples.

We first remark that a solution of the electromagnetic equations, giving the field at any point P and time t , due to a point electron moving in any manner can be obtained, as is well known, in terms of two potentials of the form,

$$\phi = \frac{C^2 e}{\left[r \left(1 - \frac{\mathbf{V}_r}{C} \right) \right]}, \quad \mathbf{A} = \frac{e [\mathbf{V}]}{\left[r \left(1 - \frac{\mathbf{V}_r}{C} \right) \right]},$$

where r is the distance of the point P , not from the position O of the electron at the time t , but from some other point O' previously occupied by the electron, and so situated that the time taken by the electron to go from O' to O is the same as the time taken by light to travel from O' to P . $\mathbf{V}$ is a vector representing the velocity of the electron when at O' , and $\mathbf{V}_r$ is the component of $\mathbf{V}$ resolved along $O'P$. The vectors $\mathbf{F}$ and $\mathbf{H}$, representing the ætherial displacement and magnetic vectors respectively, are related to the scalar and vector potentials ϕ and $\mathbf{A}$ by the equations

$$\mathbf{F} = -\dot{\mathbf{A}} - \text{grad } \phi, \quad \mathbf{H} = \text{rot } \mathbf{A}.$$

Now suppose we have a single electron, alone in empty space, describing a closed orbit s_1 . We may say that this is impossible without a distribution of electrons of opposite sign inside the orbit; there is no doubt, however, that algebraical functions of x, y, z , and t exist, satisfying the electromagnetic equations, and corresponding to this single electron, for no matter how the electron may be supposed to move, we can, theoretically, at each instant write down the values of ϕ and $\mathbf{A}$ corresponding to the case, the difficulties involved in so doing being merely algebraical. The values of the ætherial displacement and magnetic vectors obtained in this way

* See 'Theory of Electrons,' by Lorentz, p. 50.

certainly satisfy (1). Let us imagine them expressed as functions of x, y, z, t , and let us denote them by f', g', h', a', b', c' . Now let us imagine another electron moving in some orbit s_2 , the first being absent, and let the field of the electron when expressed in terms of x, y, z, t , be denoted by $f'', g'', h'', a'', b'', c''$. Now it is an algebraical fact that if the functions f', g', h', a', b', c' , and $f'', g'', h'', a'', b'', c''$, satisfy (1), the functions $f' + f'', g' + g'', h' + h'', a' + a'',$ &c. also satisfy (1), which means, that if the two electrons are brought into each other's vicinity, we can imagine them to describe orbits of the same shape as those which they described when alone, and we shall obtain a solution of the electromagnetic equations corresponding to this case by simply adding the fields which the electrons would produce if alone. We have to make no special adjustments in the fields in order to keep the flux round each electron constant, because the surface integral of the ætherial displacement due to one electron gives a zero effect when integrated round the other. This solution would of course mean that the two electrons were producing no action on each other. We may on this line of argument imagine any number of electrons moving about in the vicinity of each other, and if we add the fields corresponding to each electron when moving in its present manner, but out of the vicinity of the others, we obtain a solution satisfying the electromagnetic equations, each electron apparently moving independently and uninfluenced by the others. A simpler example is afforded by considering two electrons moving with constant velocity v along the axis of x , and separated by a fixed distance. If we simply add the known fields corresponding to these two electrons when moving separately, we shall obtain a solution of the electromagnetic equations which will be consistent with the electrons moving in the manner stated for all time, and yet we know that they would not do so, they would repel each other.

These examples suffice to show that it is not sufficient to say that because a system satisfies the electromagnetic equations, it is a system which can actually exist. Of course, if at any instant we are given, at all points, the actual field of a system which really *can* exist, the electromagnetic equations will determine for all time the subsequent and previous history of the system, for the time rates of change of f, g, h are, at each instant, given in terms of the spacial derivatives of a, b, c , and an analogous remark applies to the time rates of change of a, b, c . If we were to start from any actually existing system of electronic motions, and try to separate an electron out and cause it to move by itself in the path denoted

by s_1 , and with the field corresponding to that motion (*i.e.* without other charges or fields constraining it to do so), we should find the operation impossible. When we speak of separating the charge out in this way, we must imagine the operation to be performed entirely by electromagnetic agency, the very atoms of our imaginary fingers are parts of the electromagnetic system, and the action of separating the electron out is one which must be supposed to have been anticipated in the system for an infinite time back, and to have arisen out of the spontaneous changes in the system as a whole.

Again, we should find it impossible to imagine a set of *actual* spontaneous electromagnetic changes, by which the fields of the two electrons moving along the axis of x in the example above quoted could be brought into the state there suggested after all other fields had been removed, at least, if we did find it possible to get them into this state, *from an actually existing state*, it would mean that the electromagnetic equations were inconsistent with facts. If we inquire why it is that, of all the conceivable states of electronic motions satisfying the electromagnetic scheme only certain types are found in practice, the electromagnetic equations have nothing to tell us. If we give them an actual system to manipulate, they can tell us its subsequent and previous history, but they are unable to tell us, for example, why it is that two electrons when alone cannot continually follow each other with constant velocity, or why a single electron cannot move by itself in a closed curve.

Of course, in other branches of physical knowledge we form other laws, founded on experiment, which specify more precisely the types of motion which can exist; for instance, laws of motion involving the conception of forces between point singularities would tell us that the above system of two point charges following each other with constant velocity was an impossible one. Again, the tangential surface condition introduced in the consideration of problems on charged conductors, involves a restriction on the types of field which can occur, affording as it were a means by which one body can act on another. A few remarks must here be made on the position occupied by these "Subsidiary Laws," as we shall call them, in a scheme which takes the electromagnetic equations as a basis.

If at some instant we were given the complete field at every point in the universe, we should require no subsidiary laws at all, the electromagnetic equations are themselves sufficient, as we have already remarked, to tell us the complete past and subsequent history of the system, every action and every

experiment which ever had or ever would take place being completely determined. It would be hopeless, and in fact needless, for us to inquire how the system originated, or why it was that the present system was started rather than some other, equally consistent with the electromagnetic scheme, but showing types of motion which can never naturally evolve out of the present universe. Since we cannot ascertain the complete field of the universe at some instant, we are obliged to fall back on more crude observation, and formulate certain subsidiary laws which are broad enough to restrict the types of field and of electronic motions which are to be considered as possible, to those which it is possible for the electromagnetic scheme to evolve out of the actually existing universe, that is to say, to those fields and motions which we actually find in practice*. These laws are of course to be of such a nature as never to clash with the electromagnetic scheme, which, as we have seen, is sufficient in itself to tell us the subsequent history of a system when once that system is completely specified for some instant. These subsidiary laws are in fact hardly entitled to be called fundamental laws at all, being merely substitutes for what we lack in being without complete knowledge of the field of the universe at some instant. The great practical difficulty consists in formulating the true nature of these subsidiary laws, which usually resolve themselves into sets of more or less approximate truths, sufficiently accurate for the particular purpose in hand. To illustrate this point suppose we were to attempt to say what would happen if two similarly charged spheres were placed near to each other and left to themselves. Without further data it is impossible to give any answer to the question. The electromagnetic scheme would be satisfied if we were to say that the spheres remained at rest, and gave as the field the sum of the fields due to each sphere when alone. To proceed any farther in our problem it is necessary to partially make up for our deficiency of knowledge of the electronic motions in the sphere by the application of some tangential surface condition. Still we shall be able to find an infinite number of solutions to fit the case, and it becomes necessary to introduce the idea of a Newtonian mass †, together with the accompanying notions of forces and ordinary dynamical laws, and even then our solution will be indeterminate without specification of the

* On this view, gravitation, for instance, occupies the position of one of the "subsidiary laws," being a kind of empirical expression of a property of matter really inherent in the nature of the electronic fields, and motions originally started.

† The introduction of the idea of Newtonian mass is only necessitated by the deficiency of our knowledge of the electronic distributions and motions in the molecules of the sphere.

initial state of the field and of the oscillations on the spheres, which of course depend on the manner in which they were originally brought into the vicinity of each other.

Returning now to the problem of uniform translation, we see that we are not justified in saying that the solution suggested by the transformation is one which could possibly have arisen out of the system S . The transformation simply tells us that if S satisfies the electromagnetic scheme, S_1 also satisfies it, but so would a system of electrons moving in orbits of similar shapes to those of S_1 but all slightly or in fact completely separated out, instead of being pushed together, for the total solution in any configuration of the system is simply the sum of the solutions which we should obtain by considering each electron as moving independently in its orbit, and we can put the orbits wherever we please, and by adding the independent solutions obtain a solution of the electromagnetic equations. We may even, if we wish, imagine the orbits altered in shape. In fact, it seems that the transformation, by itself, tells us astonishingly little; it simply tells us that if one solution of (1) exists, it is possible to find another corresponding to the same electrons, but then we can theoretically write down the solution corresponding to the electrons moving in any orbits and in any manner we choose to assign, and the solution given by the transformation possesses no unique advantage in that it reduces to the solution for the system at rest when we put v equal to zero, for we can imagine any number of types of electronic motion, *only differing from the motions in the system at rest by functions of the velocity v , which vanish when v is put equal to zero*, and we can always, as we have seen, find the field consistent with these motions. Even considering a molecule in the system at rest; though the field in that molecule certainly is consistent with the electromagnetic scheme, we can realize how far this is from being the sole factor in the determination of the electronic motions, and how large a part is played by what we have termed the subsidiary laws, when we observe that as far as compliance with the electromagnetic scheme is concerned, the electrons in the molecule might move in any paths we choose to assign.

The objection here raised against the solution given by the transformation is on a different plane to objections which might at first sight be raised against the solutions of many dynamical problems, in which the final solution is obtained so as to satisfy certain conditions without inquiry as to the mode of transition from one state to the other, for in those problems the conditions are usually such as to completely restrict the final solution to one, and only one form. In dealing with

the problem of uniform translation, however, it certainly seems that we must either introduce a sufficient number of what we have termed subsidiary laws, to completely restrict the moving system to one type in its relation to the fixed system, quite apart from the consideration as to whether the motions in it could have arisen out of the fixed system, or, must specify completely the state of the field, and consequently of the electronic motions in the system at rest, and also the exact electromagnetic procedure by which the translatory motion is imparted, for in the general case the final result will depend on these *. Specification of the electronic motions in the system at rest corresponds in part to a statement of the elastic properties of the material, and the determination of the solution of our problem without specification of these motions would be, in general, as impossible, as would be the determination of the extension of an elastic thread when swinging round with a weight at the end, if we were without knowledge of the elastic properties of the thread.

The University of Sheffield,
June 30, 1911.

VII. *On the Spectrum of the Magnesium High-frequency Arc.*
By ELLEN O'CONNOR, B.Sc.†

[Plate V.]

THE element magnesium shows, probably to a greater extent than any other element, changes in the spectrum according to the various means adopted for bringing the substance into the state of incandescent vapour. This and also, as Kayser points out, its astronomical importance have led to numerous investigations on the behaviour of magnesium under varied conditions of electrical discharge. The high frequency discharges hitherto employed depend upon the oscillatory discharge of a leyden-jar, and are therefore of the nature of *damped* oscillations. The electrical conditions in such a discharge are very complex and not yet fully understood. It seemed of interest, therefore, to examine the spectrum of an *undamped* oscillatory discharge such as can now be produced by the methods employed in wireless telegraphy.

Apparatus.—The generator employed was of the Poulsen

* Ordinary electrodynamical principles, involving the conception of forces between the singularities, make the effects produced in the system, by the translatory motion, depend on the electronic motions in the system at rest, the solution corresponding to that given by the transformation only following as an approximation, for the case of very slow orbital motions.

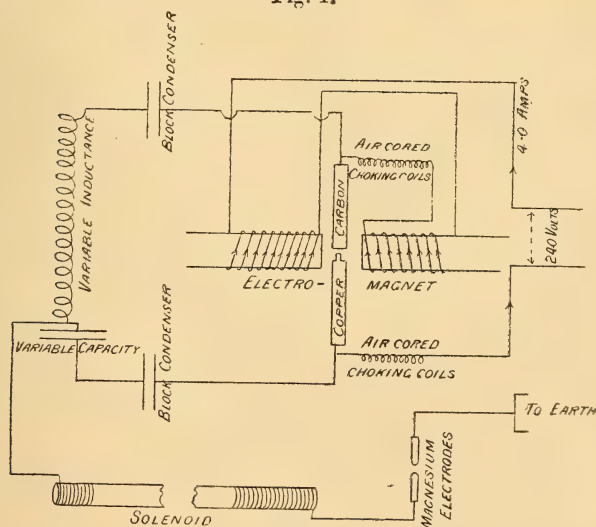
† Communicated by the Author.

type as previously * used in an investigation of the Poulsen arc. The arc was struck between horizontal electrodes of copper and carbon in an atmosphere of coal-gas and in the field of a powerful electromagnet.

The supply current of about 4 amps. was taken from the public supply at 240 volts. An oscillatory circuit consisting of a variable inductance wound with thick copper rod ($\frac{1}{2}$ in.) and a variable leyden-jar battery formed a shunt to the arc, large capacity block condensers being inserted to cut off the supply volts from this circuit. When large choking-coils were included in the arc supply circuit and the copper anode was water-cooled no difficulty was experienced in maintaining continuous oscillations for as long as was desired.

If a piece of metal or carbon held in the hand or earth-connected is brought into contact with the terminal of the inductance which is joined to the capacity, an arc of 1 or 2 cm. in length can be drawn out and maintained. Observations with a wave-meter showed that this discharge had

Fig. 1.



practically the frequency of the undisturbed oscillatory circuit. We have, therefore, an arc which consists of a variable high-frequency discharge of undamped oscillations which can be produced between any selected electrodes. A preliminary examination of an arc produced in this way was the subject of the present investigation. Fig. 1 shows diagrammatically the disposition of the apparatus.

* E. O'Connor, *Phys. Zeit.* vol. xii. p. 196 (1911).

The magnesium electrodes were held in clamps on an adjustable stand, one electrode being connected to the junction of the inductance and capacity in the oscillatory circuit, the other being earth-connected through a hot wire ammeter. The generator having been started, the electrodes were brought into contact and an arc struck. The length of the arc which can be maintained with magnesium depends upon the conditions in the oscillatory circuit, and in the following experiments was from 1 to 3 mm. With a frequency of 10^5 per sec. the current, as measured by the hot wire ammeter, was 0.8 amp. Increasing the frequency causes a decrease in the arc-length and current. With a frequency of 6.5×10^5 per sec. the current falls to 1/10 of its original value and an arc can only just be maintained.

The light from this arc was concentrated by means of a condenser on to the slit of a Hilger fixed-arm spectrograph. As the prism of this spectrograph was of very dense glass it was not possible to photograph the spectrum below a wave-length of 4000. By making use of panchromatic plates* the spectrum could be obtained between the wave-lengths 6570 and 4000.

Pl. V. fig. 2e shows a typical spectrum of this form of high-frequency arc which, for the purpose of comparison, was photographed on the same plate as the spectrum of the direct arc (fig. 2b) and that of a leyden-jar discharge through a large inductance (fig. 2c), the same electrodes being used in each case. It will be seen that there is a marked difference between the spectrum of the undamped high-frequency arc and that of the direct arc and spark. One interesting feature is the intensity of $\lambda 4481$. If the relative intensity of this line can be taken as a criterion of the temperature in the arc it would appear that this high-frequency arc was intermediate to the ordinary arc and spark†. It is more probable, however, that the low current density is responsible for its intensity.

The conditions in the oscillary circuit were next varied to see if these differences could be accentuated, and to trace if possible the cause of any changes produced.

A short visual examination of the spectrum showed that variations could easily be obtained. With a frequency of 10^5 per sec. the spectrum consists of a few lines on a continuous background, while at the higher frequency of 6.5×10^5 per sec. it becomes richer in lines, the continuous spectrum has disappeared to give place to a feeble band spectrum (nitrogen). The change in the appearance of the

* Wratten and Wainwright.

† Kayser, *Astron. Nachr.* clxii. pp. 277-282 (1903).

spectrum is gradual, not in the sense that the new spectrum continuously strengthens at the expense of the old one, but as the frequency is increased the spectrum tends to become unsteady, the continuous spectrum disappears and new lines come up intermittently; as the frequency is further increased the second spectrum predominates, and the first one comes up intermittently, finally disappearing as the frequency is further raised.

If an Oudin coil in the form of a solenoid of 2500 turns of 3.4 cm. diameter and 1 metre long is placed between the oscillatory circuit and the arc, thus raising the voltage and diminishing the current strength, the character of the spectrum is again changed. The nitrogen band spectrum is visible and the metal lines weakened even at the low frequency. With a high frequency and high voltage the spectrum consists of the band spectrum, the "b" triplet, and $\lambda 4481$.

That the current density is an important factor in the changes is suggested by the effect that the shape of the electrodes has upon the spectrum. At the low frequencies pointing the electrodes causes only an increase in the continuous spectrum, but at the higher frequencies it tends to accentuate the characteristic appearance of these spectra. Owing to the wearing away of the electrodes it was necessary to file the ends periodically, but care was taken to keep the shape as nearly constant as possible during the experiments.

Photographs were taken of the spectra obtained with various values of inductance and capacity in the oscillatory circuit, with and without the Oudin coil in the arc circuit.

In examining the photographs the instability of the spectra in certain cases must be remembered, the photographic record being often of an integral nature, and it is possible that lines which come up intermittently but brightly may make a greater impression than feebler but more persistent ones.

The following table shows the values of the inductance, capacity, and frequency in the oscillatory circuit for the various photographs:—

	Inductance in centimetres.	Capacity in microfarads.	Vibrations per second.
<i>d, j</i>	163,200	0.01245	1.117×10^5
<i>e</i>	„	0.0020	2.787×10^5
<i>f, k</i>	„	0.00101	3.921×10^5
<i>g, l</i>	82,410	0.0020	„
<i>h, m</i>	30,710	„	6.424×10^5
<i>i, n</i>	58,490	0.00101	6.55×10^5

A comparison of the photographs *d*, *e*, *f*, *g* (Pl. V. fig. 2) in the order given shows a gradual change in the spectrum. The continuous background decreases, the lines become sharper and more numerous. Since in the cases *d*, *e*, and *f* the inductance in the oscillatory circuit is constant, and in the cases *e* and *g* the capacity is the same, the change cannot be regarded as due to variation of inductance or capacity alone. The order of these spectra is, however, the order of increasing frequency of the oscillations, and since the current through the arc varies inversely as the frequency (approx.), one or both of these are to be regarded as associated with the change in spectrum.

In those cases where there is a great difference in frequency, such as in *d* and *g*, where the frequencies are in the ratio $1 : 3\frac{1}{2}$, the differences in the spectra are considerable, while in *g* and *i*, where the frequencies are in the ratio $1 : 1\frac{1}{2}$, the spectra are the same.

In the low-frequency arc, when the oscillatory circuit has an inductance of 163,200 cm. and a capacity of .01245 mfd., the spectrum consists principally of the *b* triplet, the line 4481, the oxide fluting which is somewhat lost in the continuous background, and four lines 5528.75, 4703.33, 4352.18, 4167.81 of the Rydberg* series.

Any alteration in the oscillatory circuit within the limits used in these experiments appears to have little effect upon either the *b* triplet or the line 4481. They always remain the strongest lines in the spectrum, their intensities being approximately equal. The lines of the series become sharper and stronger with increase of frequency. This can be seen in *d*, *e*, *f*, *i* (Pl. V. fig. 2), where the frequencies were 1.1×10^5 , 2.7×10^5 , 3.9×10^5 , and 6.5×10^5 .

In the case of the lowest frequency all the lines, with the exception of 5528, are diffused towards the red end of the spectrum, as in the case of the spark, and still more in the direct-current arc at atmospheric pressure (Pl. V. fig. 2).

With rise of frequency this diffusion disappears. If the frequency is kept constant and the capacity and inductance varied, there appears to be no alteration in the intensity of the lines. Photographs *f* and *g* show the spectra of the arc when the capacity in the oscillatory circuit was .00101 mfd. and .002 mfd. respectively, the corresponding inductances being 163,200 cm. and 82,410 cm., the frequency in each case being 3.9×10^5 per sec.

A distinctive feature of the high-frequency arc-spectra is

* Rydberg, Wied. *Ann.* l. p. 625 (1893), lii. p. 119 (1894).

the presence of two pairs of lines at wave-lengths 4385, 4391 and 4428, 4434 *.

These lines are ill-defined in the ordinary spark, but appear distinctly when a small amount of inductance is introduced into the discharge circuit, disappearing, however, when the inductance is increased. In the high-frequency arc these lines do not appear at the lower frequency of 1.1×10^5 per sec. when the inductance is 163,200 cm., but when the frequency is raised to 3.9×10^5 by reducing the capacity only slight traces of the lines appear. On increasing the frequency by decreasing both capacity and inductance the lines become still more prominent. If the frequency is kept constant and capacity and inductance varied, the lines are strongest for the smallest value of the inductance.

Brooks † in his high- and low-frequency experiment found that if in the high-frequency discharge the thin electrodes were replaced by thick rods, the lines (F and P) were still present, but not the hydride spectrum, except that after long running traces of the head of the band 5210 appeared. Comparing the conditions of the high- and low-frequency discharge in Brooks's experiment, the introduction of the leyden-jar increases both frequency and current density. Brooks considers the current density to be the factor governing the presence of the lines. With the undamped high-frequency arc the lines were absent at the low-frequency and high-current density, but when the frequency was raised by decreasing the capacity, and consequently decreasing the current density, the lines appeared. This suggests that the presence of the lines is governed by the frequency rather than the current density.

The only indication of the hydride is a trace of the head 5210 (lens), which, like the F and P lines, is to be seen in the spectra given by the higher frequencies (Pl. V. fig. 2, *f, g, h, i*). If the arc is taken in an atmosphere of coal-gas the band becomes very intense, and the carbon fluting at 4315 is strong. No connexion between the line 4571 and the hydride spectrum was observed. In view of the fact that Brooks associates the presence of this line with the formation of a nitride, it is of interest to notice that the conditions in the oscillatory circuit which give this line with the greatest intensity at the low potential are those which give the best

* A. Fowler and H. Payn, *Proc. Roy. Soc.* lxxii. p. 253 (1903).

† E. E. Brooks, *Proc. Roy. Soc.* lxxx. p. 223 (1908).

nitrogen-band spectrum, when by the introduction of a solenoid the higher voltage is used.

At the high voltage an arc of several mm. length can easily be maintained, but the intensity of the light dies out rapidly with increase of length. The length used in these experiments was between 2 and 3 mm.

The lines of the series, 5528, &c., are sharpened but much weakened in intensity, and die out as the frequency is raised (Pl. V. fig. 2, *j, k, l, m, n*). The trace of the positive-band spectrum of nitrogen which was only slightly visible at the lower potential becomes much more prominent. At the lowest frequency used (1.1×10^5 per sec.) it is not easily obtained. It comes up intermittently and dies out leaving a continuous background with only a few magnesium lines and the oxide fluting at 5007. The intensity of the nitrogen spectrum is roughly in inverse proportion to the intensity of the other lines. This is especially applicable to the oxide fluting, which was never found to be present at the same time as a good nitrogen-band spectrum. At the higher frequencies, when the bands have become the most prominent part of the spectrum, all traces of the oxide have disappeared, and the spectrum consists almost entirely of the nitrogen bands, the *b* triplet, H_{α} , and the line 4481. At these frequencies the current through the arc is very small and unsteady. The light is consequently feeble and the spectrum can only be seen intermittently, the lines not all disappearing at the same time. It will be noticed that the most refracted line of the *b* triplet is very faint (*m, n*). Visual observations showed that during the fluctuations of the light this was the least persistent component of the triplet. At the same time the presence was noted of several fine lines in the neighbourhood of the triplet, some of which appear on the photographs (*n*). These may be some of the lines of the fluting already measured by Eder and Brooks, although their appearance suggests a possible connexion with the F and P lines and the associated ultra-violet lines. The wave-lengths could not be determined accurately enough to enable a connexion between the frequencies to be established with certainty.

There are also several lines which could not be identified between the oxide fluting at 5007 and the *b* triplet, which, like the above pairs, are seen in the high-frequency spectra at low voltages. At both high and low voltages a line was visible though not strong at 6160. It is intensified by the high voltage. Several variations in the mode of producing these spectra have been tried, including an air-blast directed

against the arc, the only result observed being a weakening of the oxide spectrum. The experiments described above are of a preliminary nature, and it is hoped to continue the work.

I wish to express my indebtedness to Mr. Morris-Airey for suggesting the experiments and for his valuable advice.

Physical Department, Armstrong College,
Newcastle-upon-Tyne.

VIII. *The Law of Molecular Attraction.*

*By D. TYRER, M.Sc.**

THE nature of molecular attraction is a problem which has at various times attracted a considerable amount of attention. The question is involved in the study of energy changes connected with surface tension and isothermal volume changes. Knowing the law of molecular attraction, it is easily possible to deduce a formula to represent the relation between the potential energy of a liquid and its density, as for example the relation between latent heat of vaporization of a liquid and its density. Assuming that the attraction between two molecules varies inversely as the square of the distance between them, an equation involving the latent heat was deduced by J. E. Mills † which holds remarkably well. This equation may be written

$$\frac{L-E}{D_L^{\frac{1}{3}}-D_V^{\frac{1}{3}}}=\mu,$$

where L is the latent heat of vaporization, E is the external work done during vaporization, D_L and D_V are the densities of liquid and saturated vapour respectively, and μ is a constant dependent only on the nature of the liquid. Because this relation fits the facts it was thought by Mills that the assumed law of attraction was the true one; but this by no means follows ‡.

Kleeman § has deduced the following formula for the law of molecular attraction:

$$\phi\left(\frac{z}{x_c} \cdot \frac{T}{T_c}\right) \frac{(\Sigma \sqrt{m_1})^2}{z^5},$$

where z is the distance of separation of the molecules, $\Sigma \sqrt{m}$

* Communicated by the Author.

† Journ. of Phys. Chem. vi. p. 209; viii. pp. 385, 593; ix. p. 402; xi. pp. 594, 132.

‡ Vide Kleeman, Phil. Mag. Jan. 1911, p. 83.

§ Phil. Mag. xix. pp. 783-809 (1910).

is the sum of the square roots of the atomic weights of the atoms of the molecule, x_c is the distance between the molecules at the critical temperature T_c . The function $\phi\left(\frac{z}{x_c} \cdot \frac{T}{T_c}\right)$ is unknown, but is constant at corresponding temperatures. This formula makes the law of attraction dependent both on the distance of separation of the molecules and on the temperature.

Van der Waals in his equation of state

$$\left(P + \frac{a}{v^2}\right)(V - b) = RT,$$

by introducing the term $\frac{a}{v^2}$ supposes the attraction of the molecules to vary inversely as the fourth power of their distance of separation. But, as is well known, this is insufficient, as the term $\frac{a}{v^2}$ does not, with liquids, adequately represent the facts.

Now, as has been already mentioned, it is supposed by Kleeman that the law of attraction varies with the temperature. It is, however, very difficult to see how a force of attraction acting between two molecules should be in any way influenced by their velocity or kinetic energy, which of course really represents their temperature. Kleeman has suggested * that the atoms in a molecule are in a state of rapid motion round the centre of gravity, and that the centrifugal forces thus set up are balanced by atomic attractions, and further that the effect of increase of temperature is to disturb this balance and to alter in this manner the force of attraction at a given external point. This hypothesis is untenable from two considerations. In the first place, it is highly improbable that the atoms in a molecule are in a state of rapid motion relative to one another; for it is hardly conceivable that in a very complex molecule under normal conditions, the atoms could maintain their relative positions with such perfect regularity as the theory of stereochemistry demands. It is probable that, at ordinary temperatures, the molecules of stable substances have no other kinetic energy than that of rotational and translational motion. In the second place, the explanation involves the assumption that atomic attraction is identical with molecular attraction, but there appears to be little or no connexion between the two. The force of attraction which causes the union of, say, an atom of hydrogen with an

* Phil. Mag. Jan. 1911, p. 93.

atom of chlorine is far greater than any molecular force of attraction, while the attraction between a molecule of hydrogen and a molecule of chlorine is extremely small. Furthermore, it is impossible to discover any additive law resolved to atomic attractions, to represent the attraction between two molecules. It is necessary to assume that the atomic attractions neutralize one another, whereas there is every evidence for the supposition that the attraction exerted on an external molecule by two adjacent molecules is double the attraction between the external molecule and one of the molecules. Kieeman * has sought evidence for the relation between atomic and molecular attraction by deducing certain relationships between the physical properties of members of homologous series. But it can be shown that almost every physical property or combination of properties of the members of a homologous series is proportional to some function of the molecular weight. As far as latent heats of vaporization and their relation to molecular attraction are concerned, it will be shown in this paper that it is not necessary to assume that the formula representing the law of molecular attraction includes a temperature function.

Let us suppose for the present that the force of attraction between two like molecules depends only upon their distance of separation. We may represent it by

$$\frac{K^2}{S^n},$$

where K is a constant dependent only on the nature of the molecules, S is their distance of separation, and n is a small number to be determined. Consider a finite mass of a normal unassociated liquid, with the molecules evenly distributed in space. The attraction between any pair of molecules is

$$\frac{K^2}{(C_1 S)^n}, \text{ and between a second pair of molecules } \frac{K^2}{(C_2 S)^n}, \text{ say.}$$

Suppose now that the liquid expands isothermally until the distance between two adjacent molecules is S_1 . It is obvious that if the geometrical form of the mass of liquid remain the same, the terms $C_1, C_2, \dots$ &c. are constants.

The total work done by the separation of all the pairs of molecules is

$$\begin{aligned} & \frac{K^2}{C_1^{n-1}} \int_s^{S_1} \frac{dS}{S^n} + \frac{K^2}{C_2^{n-1}} \int_s^{S_1} \frac{dS}{S^n} + \frac{K^2}{C_3^{n-1}} \int_s^{S_1} \frac{dS}{S^n} + \dots \&c. \\ & = \frac{K^2}{C^{n-1}} \int_s^{S_1} \frac{dS}{S^n} \Sigma \left(\frac{1}{C^{n-1}} \right) = W, \text{ say.} \end{aligned}$$

* Phil. Mag. xx, p. 905 (1910).

W represents total work done against molecular attraction during the expansion of the liquid. Integrating, we have

$$W = C \left(\frac{1}{S^{n-1}} - \frac{1}{S_1^{n-1}} \right), \quad . \quad . \quad . \quad (1)$$

where $C = \frac{K^2}{n-1} \cdot \Sigma \left(\frac{1}{C^{n-1}} \right)$, and is a constant dependent only on the nature of the liquid. In deducing this equation for the isothermal change of potential energy of an expanding liquid, the usually accepted assumptions in regard to molecular energy have been made. On account of their importance in the later portion of this paper these assumptions may be stated here.

(1) The kinetic energy of the molecules of a liquid or gas is independent of the volume.

(2) When a liquid expands isothermally, the energy absorbed goes entirely to do (a) work of expansion against molecular attraction, and (b) work of expansion against an external pressure.

(3) The total attraction exercised by a group of molecules on a single external molecule a certain distance away is the sum of the attractions exercised by each of the molecules separately.

If V_1 and V_2 are the volumes of the liquid before and after expansion, and if work is also done against an external pressure $p = \phi(V)$ which varies from $p_1 = \phi(V_1)$ to $p_2 = \phi(V_2)$, equation (1) becomes

$$W = C \left(\frac{1}{V_1^{\frac{n-1}{3}}} - \frac{1}{V_2^{\frac{n-1}{3}}} \right) + \int_{V_1}^{V_2} \phi(V) dV, \quad . \quad . \quad (2)$$

where S has been put equal to $V^{\frac{1}{3}}$.

If we consider the case of the expansion of a liquid to the state of vapour, equation (2) becomes

$$L = C \left(\frac{1}{V_L^{\frac{n-1}{3}}} - \frac{1}{V_v^{\frac{n-1}{3}}} \right) + E, \quad . \quad . \quad . \quad (3)$$

where L is the latent heat of vaporization, V_L and V_v are the specific volumes of liquid and saturated vapour respectively, and E is the external work done during the vaporization. Now we might apply this equation to the determination of n by substituting for L , E , V_L and V_v their values at different temperatures for a given liquid; but the value of n thus obtained would not necessarily be the true value. For example, when n is put equal to 2 or 7, two equations are obtained both of which fit the facts equally well*. But if

* *Vide* Kleeman, Phil. Mag. Jan. 1911, p. 83.

we know three points on an isotherm of the equation

$$W=f(V),$$

where W is the internal work of expansion and V is the volume, we can completely determine n by the application of equation (1).

Consider unit mass of a normal liquid at volume V and temperature T . Imagine it to expand isothermally under a negligibly small external pressure until the volume has increased by an amount ΔV equal to the increase in volume when the liquid is heated over a range of one degree. The work done must be given by

$$W=C_p-C_v,$$

where C_p and C_v are the specific heats of the liquid at constant pressure which is relatively small and at constant volume respectively. We then obtain the equation

$$C_p-C_v=C\left\{\frac{1}{V^{\frac{n-1}{3}}}-\frac{1}{(V+\Delta V)^{\frac{n-1}{3}}}\right\}.$$

Now the values for C_p-C_v for liquids are not generally known, but can be calculated from compressibility data by aid of the thermodynamic formula

$$C_p-C_v=\frac{T}{J}\cdot\frac{\left(\frac{dv}{dt}\right)^2}{\left(\frac{dv}{dp}\right)},$$

or

$$C_p-C_v=\frac{T}{J}\cdot\frac{\left(\frac{dv}{dt}\right)^2}{v\beta},$$

where T is the temperature, J the mechanical heat equivalent, v the specific volume, and β the compressibility coefficient of the liquid at the temperature T .

Table I. below contains the values of C_p-C_v for some liquids calculated in this manner. Errors in these values are due principally to inaccuracies in the experimental data for β and $\frac{dv}{dt}$. In some cases, the values of β have

been obtained by extrapolation of results at pressures higher than one atmosphere. It is of course, strictly speaking, necessary to consider only values of β which refer to a pressure of one atmosphere; but data are also included in the table when the pressures at which β was determined are comparatively small.

Combining the equation

$$C_p - C_v = C \left\{ \frac{1}{V^{\frac{n-1}{3}}} - \frac{1}{(V + \Delta V)^{\frac{n-1}{3}}} \right\}$$

with equation (3) we get

$$\frac{C_p - C_v}{\left\{ \frac{1}{V^{\frac{n-1}{3}}} - \frac{1}{(V + \Delta V)^{\frac{n-1}{3}}} \right\}} = \frac{L - E}{\left\{ \frac{1}{V_L^{\frac{n-1}{3}}} - \frac{1}{V_V^{\frac{n-1}{3}}} \right\}}.$$

Neglecting for low temperatures the term $\frac{1}{V_V^{\frac{n-1}{3}}}$ as small compared with $\frac{1}{V_L^{\frac{n-1}{3}}}$, we can write

$$n = 3 \frac{\log \left(1 - \frac{C_p - C_v}{L - E} \right)}{\log \left(\frac{V}{V + \Delta V} \right)} + 1. \quad \dots \quad (4)$$

In Table II. are given the values of n calculated by aid of this equation. The values of $L - E$ are taken from tables calculated by Mills* by aid of the Clapeyron-Clausius equation.

Though the values of n appear to approximate to the value 4, they cannot be regarded as constant as the divergencies are greater than errors in the data. Moreover, the relation

$$L - E = C \left\{ \frac{1}{V_L} - \frac{1}{V_V} \right\}$$

obtained by putting $n=4$ in equation (3) does not hold. We must conclude that either (1) the equation representing the law of attraction between molecules includes some other function besides the simple function of the distance of separation of the molecules, or (2) the assumptions regarding the potential energy of a liquid on which the above equations are based are not true. Let us first consider the second possibility. One assumption which certainly requires a closer study than has hitherto been accorded to it, is that the total energy of a liquid or gas, minus the potential energy of molecular attraction and potential energy due to

* Journ. of Phys. Chem. viii. p. 405 (1904).

TABLE II.

Liquid.	T°. °	L - E.	n.
Ether	273	86.16	4.1
	283	83.44	4.0
	293	80.40	4.0
	303	77.92	4.1
Pentane	273	85.85	3.2
	293	81.0	3.1
	313	75.55	3.0
	333	71.66	3.3
	353	66.84	3.4
Heptane.....	296	81.0	4.2
Octane	296	81.5	4.3
Carbon tetrachloride ...	293	46.5	4.8
	293	46.5	4.6
Chloroform	273	62.45	3.0
	293	61.29	3.3
	313	59.00	3.2
	333	56.73	3.1
Benzene	288	97.4	4.5
	293	96.6	4.5
	303	94.7	4.4
	313	92.7	4.4
	323	91.0	4.3
Carbon bisulphide	293	80.31	4.0
	298	79.14	4.0
	291	80.57	3.7
Toluene	273	101.0 (calc.)	4.2
	293	96.6 "	4.2
	313	92.5 "	4.2
	333	88.5 "	4.3

an external pressure, is independent of the volume. The question can be tested in the following way.

If the total change of energy of a liquid which expands at constant temperature is not entirely made up of the changes in the potential energies of attraction and of external pressure, then we should expect to find that the specific heat of a liquid (or a gas) at constant volume varies with the density. Or, what comes to the same thing, that

$$C_{p\text{Liquid}} - C_{v\text{Liquid}} \neq C_{p\text{Liquid}} - C_{v\text{Vapour}},$$

where $C_{v\text{Liquid}}$ and $C_{p\text{Liquid}}$ are the specific heats of a liquid at

constant volume and constant pressure respectively, and $C_{p\text{Vapour}}$ is the specific heat of the vapour at constant volume at the same temperature.

A table of values of $C_{p\text{Liquid}} - C_{v\text{Liquid}}$ has already been given. It is only necessary to obtain values of $C_{p\text{Liquid}} - C_{v\text{Vapour}}$ and to compare the two.

In the following tables are given these values of $C_{p\text{Liquid}} - C_{v\text{Vapour}}$. The values of the specific heats of the vapours at constant volume have been obtained usually by extrapolation from experimental results for higher temperatures. The values for the specific heats of the liquids at constant pressure have been obtained as a rule by extrapolation of values at lower temperatures. Where several results by different observers were available, mean values of concordant figures have been taken. Every effort has been made to obtain as great an accuracy as possible in the comparison of the two sets of values.

Substance.	T (° C.).	$C_{v\text{Vapour}}$	Authority.	$C_{p\text{Liquid}}$	Authority.	$C_{p\text{Liquid}} - C_{v\text{Vapour}}$	$(C_p - C_v)_{\text{Liquid}}$
Chloroform.	50°	0.1245	Wiedemann	0.2373	Regnault.	0.1128	0.0560
	60	0.1258	& Regnault.	0.2383	"	0.1125	0.0557
Ether	40	0.3775	Wiedemann.	0.5763	"	0.1988	0.159 (approx.)
	20	0.276	Jaeger.	0.5527	"	0.277	0.1325
	35	0.288	Neyreneuf.	0.570	"	0.282	0.145
Carbon bi- sulphide.	40	0.112	Regnault.	0.242	"	0.130	—
	50	0.114	"	0.243	"	0.129	—
	15	0.110	Capstick.	0.236	"	0.126	0.098
	33	0.127	Beyne.	0.240	"	0.113	0.094 at 25°
Benzene	40	0.232	Regnault & Wiedemann.	0.433	Pickering & Mills & McRae.	0.202	0.130
	50	0.243		0.437		0.194	0.132
	60	0.255		0.446		0.191	0.140

On account of the lack of experimental data the above table is very incomplete. The figures given in columns 3 and 5 were not obtained directly by the authorities quoted, but have been calculated from their results. A comparison of the last two columns shows clearly that the true value of $(C_p - C_v)$ for liquids is considerably smaller than that calculated by aid of the value of C_v for the vapours of the liquids.

Further data for comparison can be obtained by use of the thermodynamic equation

$$\frac{dL}{dT} = C_{p\text{Liquid}} - C_{p\text{Vapour}},$$

or

$$C_{p\text{Liquid}} - C_{p\text{Vapour}} = \frac{dL}{dT} + \frac{2}{M},$$

where L is latent heat of the liquid, T is the temperature, and M the molecular weight. In the following table the values of $\frac{dL}{dT}$ have been obtained by smoothing the values calculated from the Clapeyron-Clausius formula by Mills* and then reading off tangent values from the curves. The above equation gives approximate results.

Substance.	Temp. Range.	$\frac{dL}{dT}$ (mean).	M.	$\frac{2}{M}$.	$\left(\frac{dL}{dT} + \frac{2}{M}\right)$.	$C_{p\text{Liquid}} - C_{p\text{Liquid}}$.
Ether	0-50	0.244	74	0.027	0.271	0.132 at 20° 0.137 at 30°
Pentane	0-40	0.199	72	0.028	0.227	0.0918 at 0° 0.0878 at 20° 0.0872 at 40°
Hexane	0-50	0.160	86	0.023	0.183	0.132 at 20°
Heptane.....	0-50	0.123	100	0.020	0.143	0.1066 at 20°
Octane	0-60	0.114	114	0.017	0.131	0.1027 at 20°
Benzene	0-60	0.143	78	0.026	0.169	0.139 at 20° 0.134 at 30° 0.133 at 50°
Carbon tetrachloride..	0-60	0.071	154	0.013	0.104	0.068 at 20°

Although the results in the above tables can only be regarded as approximate, they show clearly that the specific heat of a substance at constant volume is considerably greater in the liquid state than in the gaseous state. This means that the energy change which takes place in an expanding liquid is not due solely to potential energy of molecular attraction, but must involve a liberation of intra-molecular energy. Still further evidence of this is yielded by the experiments of Joly† on the specific heat of CO₂ at constant

* *Loc. cit.*

† *Proc. Roy. Soc. lv. p. 390 (1894).*

volume under varying pressures. The following table gives the values of C_v at different densities (Δ) of the gas for a mean temperature of 56°C .

Δ .	C_v .	Δ .	C_v .
0	0.1650	0.12	0.1954
0.1	0.1671	0.13	0.1974
0.05	0.1765	0.14	0.2014
0.08	0.1842	0.15	0.2045
0.10	0.1896		

We see again that the specific heat of a fluid at constant volume increases as the density increases, and from this it must follow that in an isothermal change in density, intra-molecular energy is liberated. This result is of extreme importance in the investigation of the potential energy of liquids and molecular attraction. It vitiates at once all conclusions regarding molecular attraction based on the assumption that during the expansion of a liquid the whole of the energy absorbed goes to do work against molecular attraction, except of course the small amount which does work of expansion against the external pressure.

The intra-molecular energy liberated during expansion will probably be a function of the volume change and of the temperature. We may write this energy $F(T, V_1 - V)$. Assuming the simple law of attraction $\frac{K^2}{S^n}$, the equation (1) for the expansion of a liquid becomes

$$\frac{W_0 + F(T, V_1 - V)}{\left(\frac{1}{V^{\frac{n-1}{3}}} - \frac{1}{V_1^{\frac{n-1}{3}}} \right)} = C_1,$$

where W_0 is the observed energy change; and equation (4) becomes

$$n = 3 \frac{\log \left\{ 1 - \frac{(C_p - C_v) + F(T, \Delta V)}{L - E + F(T, V_v - V_L)} \right\}}{\log \left(\frac{V}{V + \Delta V} \right)} + 1.$$

Now as the factor $F(T, \Delta V)$ will be negligibly small, it follows that the value of n given in Table II. must be minimum values, *i. e.* the index of the distance of separation

of the molecules in the true law of attraction must not be less than 5 about.

Since the function $F(T, V_1 - V)$ must become equal to zero at the critical temperature, it must follow that the value of C in the equation

$$L - E = C \left\{ \frac{1}{V_L^{\frac{n-1}{3}}} - \frac{1}{V_V^{\frac{n-1}{3}}} \right\}$$

must increase with rise of temperature. Now the equations obtained by putting n in the law of attraction equal to 5 and 6 give values of C which decrease as temperature increases; and when $n=7$, C remains constant with rise of temperature, and for all values of n greater than 7, C increases with rise of temperature. It would seem therefore probable that the true value of n is greater than 7. The value of C in the above equation may, however, at first decrease at low temperatures and increase at higher temperatures. Unfortunately, there is not sufficient experimental evidence to test this point.

Summarising, it may be concluded that :—

(1) So far as latent heat considerations are concerned, it is not necessary to assume that the law of attraction includes a temperature function; but it is impossible to determine completely the law of attraction from considerations of energy changes accompanying the change of volume of a liquid or gas.

(2) When a liquid or gas undergoes isothermal expansion, some intramolecular energy is liberated. This is entirely apart from energy changes due to molecular attraction.

(3) Assuming that the law of attraction can be represented by $\frac{K^2}{S^n}$, where K^2 is constant for a given pair of molecules and S is the distance between them, the value of n cannot be less than 5, and is probably greater than 7.

It is hoped in a subsequent paper to discuss the problem in its relation to other physical properties of liquids.

The Chemical Department,
The University, Manchester.
August 1911.

IX. *The Variation with Distance of the Ionization produced by Röntgen Rays.* By E. W. B. GILL, M.A., B.Sc., *Fellow of Merton College, Oxford* *.

IN connexion with the still unsolved problem as to the constitution of the Röntgen rays, it seemed worth while to make a careful set of experiments on the variation of the ionizing powers of the rays with the distance from the source, to see if the law usually assumed—that the number of ions produced was proportional to the inverse square of the distance—was correct.

The bearing of this law, if correct, upon the rival theories put forward to explain the nature of the rays—the pulse theory and the corpuscular theory—would be indecisive; but if incorrect would certainly be adverse to the corpuscular theory.

For consider a beam of rays diverging from a point forming a solid cone of rays. On the corpuscular theory (if there is no absorption) the total number of particles, whatever may be their nature, crossing any section while the rays are on must be the same. But in all the modifications of the corpuscular theory, including that of Prof. Bragg, this number alone determines the number of ions produced at the section, and therefore the ionization must be the same across every section of the beam, that is, the inverse square law must be obeyed.

The pulse theory, on the other hand, could be satisfied by any law, for although the intensity of the rays is given by the inverse square of the distance, there is no reason why the numbers of ions produced should be proportional to the intensity, though they may be.

The result of the experiments to be described was that no variation, other than errors of experiment, from the inverse square law could be detected.

The above argument shows that this result, which might have been destructive to the corpuscular theory, is indecisive; but reasons will be given later for believing that it is in some respects adverse to the pulse theory.

Arrangement of Apparatus.

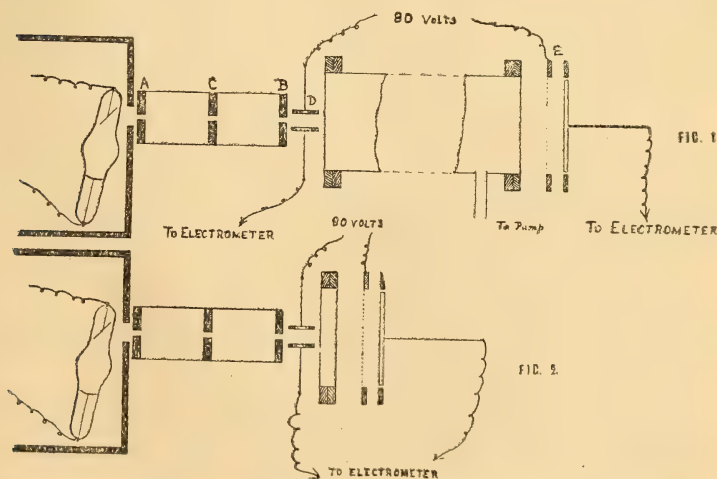
At the outset it was resolved to measure the ionization at two distances from the anode, one about four times the other; the longer distance being about 100 cm. The experimental arrangements were devised to produce a beam of rays of

* Communicated by Prof. J. S. Townsend.

circular section, which at 100 cm. from the anode would be of convenient breadth; for this breadth determines the size of the apparatus required to measure the ionization. At the same time this beam had to contain enough rays to produce a measurable ionization. The obvious method of producing a cone of rays is to allow the rays to pass through a small hole in a lead screen; but preliminary experiments showed that if the screen was near the anode, the beam was much too large at 100 cm., while if far off (of course it could not be more than 30 cm.), the ionization was not measurable unless the ions were multiplied by collision, a matter of some difficulty and inconvenience. For these reasons the idea of working with rays diverging from a very small area was abandoned.

The other points requiring attention were the elimination of absorption by the air, and to guard against accidental variations in the Röntgen ray bulb.

As a result of these considerations, the apparatus took the form shown in fig. 1. Other things being equal, the ionization can be made large by using a powerful bulb, and the one at hand happened also to be of the very convenient shape shown in the figure.



The bulb and induction-coil were contained in a lead box with a window near the anode; the primary current, which had a mean value of about 4 amperes, was taken from the town mains (100 volts) through a rough resistance and a Rotax interrupter to the coil, and the voltage across the coil

terminals averaged about 10 volts. The coil used was capable of producing an 8-inch spark.

The rays produced passed through the two circular slits in the thick lead ends of the brass tube AB; the slits were 4.5 mm. in diam., 11 cm. apart, and A was distant 10 cm. from anode; suitable screens were placed to prevent the rays leaving the box in any other direction than through the tube. A third lead disk C with a central hole of the same size was placed midway down the tube, to prevent as far as possible secondary rays from the ends and sides of tube emerging from B.

The end slits completely determined the beam of rays, and by drawing the figure to scale, or by calculation, it will be found that practically all points of the anode (which was circular, 1.8 cm. in diameter, and at an angle of 45° to line of slits) contributed radiation to the emergent beam, this being desirable for large ionization; and that at 100 cm. from anode the breadth of the beam was roughly 7 cm. On drawing the figure of rays it will be at once seen that they do not form a cone, but that the arrangement consists roughly of a cone of rays diverging from a point midway between the end slits combined with a cylindrical bundle of rays 4.5 mm. in diameter. The final result of the experiment being what it was, this arrangement is as good as any other; but had the law been different from the inverse square, it would have been necessary to devise other arrangements.

The rays emerging from B passed between the plates of a small parallel plate detector D. The plates of this were 2 cm. in diameter and 1 cm. apart, one being charged to 80 volts by small storage-cells, the other joined to an electrometer through an insulated key.

The function of this small detector was really to see that the bulb was emitting constant radiation.

The ionization produced by the beam was measured by the large parallel plate detector E, placed first in the position shown in fig. 1, and then in that shown in fig. 2.

This detector had as one plate a thin wire gauze, while the other plate was of brass placed parallel to the wires and 1.5 cm. from them. The diameter of the brass plate, which was circular, was 9 cm., thus allowing a margin of 2 cm. over the beam, which, as was mentioned, spread out to 7 cm. at the longer distance. To create a uniform field for the ions produced, a guard-ring $1\frac{1}{2}$ cm. wide enclosed this plate.

The wire gauze was charged to a potential of 80 volts, the brass plate connected to an electrometer, and the deflexion read due to the Röntgen rays being on for 1 minute. This

deflexion was always compared with that given by the small detector D under the same circumstances.

It will be noticed that the rays actually fell upon the plates of the large detector, and that therefore the ionization measured was due not only to the primary rays but also to the secondary rays given off from the plate; but as this secondary ionization is always proportional to the primary, the result gives a measure of the primary ionization. It is necessary to place this detector transverse to the rays, because the ions collected must all be sensibly the same distance from the anode, which is with this arrangement approximately the case; for instance, if the wires are 100 cm. from the anode, the ionization measured is that extending from 100 to 101.5 cm., all the ions produced in this length of the beam being collected.

The various parts of the detectors were held together by ebonite supports, and as additional precaution against leaks these were surrounded in places by tinfoil joined to earth. The remainder of the apparatus shown is an arrangement for eliminating the absorption of the air. It consisted of a long brass tube with a side tube leading to an air-pump; a shoulder was put onto each end of the tube and two rings of brass fixed to circles of aluminium could be pressed against these. If the surfaces in contact were greased, the whole formed a tube with aluminium ends which could be evacuated.

First Method of Experiment.

The original intention was to arrange the apparatus as in fig. 1, placing the large detector at say 3 cm. from the end of the tube and to compare the deflexions given by the two detectors in 1 minute, the tube being pumped to a calculated low pressure. Air was then let into the tube, which was taken away, the ends removed and placed together as in fig. 2, the left-hand one being in its original position and the large detector still 3 cm. from the other. The deflexions were again compared in 1 minute. From these results could be at once obtained the ratios of the ionizations between the plates of the large detector in its two positions.

It is obvious that the air absorption can be made the same in the two cases; for the amount of air traversed by the rays in each case can be made the same by suitably adjusting the first pressure in the tube. Any secondary radiation from the aluminiums would probably be absorbed before affecting the detectors; and even if not, the relative positions of the left-hand one and the small detector, and also the right-hand

one and the large detector, were always the same; and the error in the second experiment of radiation from the left passing through the right or *vice versa* is negligible, the aluminiums being .2 mm. thick.

Some experiments at the outset, however, proved that it was unnecessary to evacuate the tube each time.

In these experiments the large detector was kept at the longer distance (about 105 cm. from anode), and the charge received by it per minute compared with that received by the small detector for various pressures in the tube.

The small detector in these experiments after the first minute gave the same reading per minute throughout, proving that the bulb was emitting constant radiation; and this was generally the case in further sets of experiments, till the bulb in any set had been running for some time. The electrometer deflexion due to the large detector, as a mean of several experiments, was found to be the same when the air in the tube was at atmospheric pressure, half the atmospheric pressure, and at a pressure of 4 cm. of mercury; thus proving that the air absorption was negligible. The total length of the tube was about 76 cm., and in general this would produce an appreciable absorption; for instance in some experiments of Rutherford * the rays lost 1 per cent. on traversing 10 cm. of air.

The above results, however, are explained by the fact that the bulb used was rather hard, producing a very penetrating radiation, and any easily absorbed radiation would probably be stopped at the first aluminium. Further experiments showed that the rays lost about 27 per cent. in going through .4 mm. of aluminium.

The method adopted in this first set of experiments was to make two observations with the large detector, then two with the small, then four with the large, followed by two more with the small, ending up with two with the large.

The electrometer gave about 200 mm. deflexion for 1 volt, and the readings due to the large in 1 minute were about 40 mm., and to the small 35 mm. The voltage applied to the parallel plates, 80 volts, was always sufficient to produce saturation.

The above method of experiment was adhered to with slight variations in all cases, and any change in the constancy of the radiation could be at once detected.

It was thought worth while at this stage, to try whether water vapour had an exceptional absorbing effect for Röntgen

* Phil. Mag. xliii. p. 241 (1897).

rays as it has for ultra-violet light, and the tube was filled with air which had been bubbled through water both cold and warm; but in neither case could any absorption be found.

These preliminary experiments showed that the evacuated tube was unnecessary; but the general arrangement was retained without exhausting the tube for the following reason:—

It was found that the number of ions collected per minute by the small detector was liable to vary in an erratic manner when the aluminiums were away; and this was discovered to be due to accidental distortions of the electric field, but the field could be rendered steady by keeping the left-hand aluminium always in place [all the tubes were kept earthed]. Even then the presence of the large detector, if it were charged, in the nearer position seriously affected the field of the small one; and therefore to ensure the small detector always collecting ions from the same region, the large one had all its parts earthed whenever the small one was in use. The presence of the right-hand earthed aluminium also exercised a steadying effect upon the large detector; for this, although it had a guard-ring, was from its size very susceptible to induced charges, and it had finally to be surrounded on all sides except the front by an earthed metal case. It then worked in a very consistent and satisfactory manner.

Final Results of Experiments.

The mean of the experiments for the shorter distance when the wires of large detector were 24 cm. from anode gave that the ratio of the charges collected by the large and small detectors in any time was 1.08, which was correct, taking the extreme variations to 5 per cent.

For the longer distances when the wires were 98 cm. from the anode, this ratio came out to 1.04, with a slightly less variation of about 4 per cent. The variations were generally due to the fact that the ionization produced when the current was first turned on and the bulb cold, was generally larger than when it was turned on for 1 minute for later observations; in some cases these first readings were omitted in taking the mean; the primary current through the induction-coil too often varied in the course of a minute by .1 ampere, which must also produce slight errors. This current was in general 4 amperes.

Discussion of Results.

Taking into account all the possible errors, it seems that the above result shows that the ionization in 1.5 cm. of a beam 24 cm. from anode is almost exactly the same as at 98 cm. from anode, and the mean distances of these portions are approximately 1:4.

Even if the rays all diverged from a point on the anode, this would mean that the number of ions produced by rays of intensity I acting on air of volume V is the same as those produced by intensity $\frac{I}{16}$ on volume $16V$.

The discussion of the form of the beam shows that the factor 16 should probably be much larger.

Now, as pointed out at the beginning, this result is in perfect agreement with the corpuscular theory; and in the present state of our knowledge will also satisfy the pulse theory, merely leading to the fact that the number of ions produced in unit volume is proportional to the intensity.

Any conception, however, of the action of an electromagnetic pulse in forming ions from a neutral molecule must eventually result in the notion of the ions being torn out of the molecules by the forces in the pulse, certain molecules being at the instant in a more favourable condition for this than others, as only a small proportion are ionized, and obviously a certain minimum force is necessary for this; at the best, then, the inverse square law can only hold up to a certain distance, and for large distance there should be a rapid falling off from this law. In the experiments described the square of the force in the pulse was diminished to at least one sixteenth of its maximum value without an appreciable change in the number of ions produced in the beam.

The question really resolves itself into whether the minimum force required to produce ionization on the pulse theory has been approached in this experiment; and in this connexion the experiments of I. O. Griffith* are of interest. He studied the ionization produced by ultra-violet light falling upon a zinc plate which, if the pulse theory be true, must be much the same sort of action as that of the Röntgen rays producing ions in a gas. Taking those of his distances which correspond most closely to the 24 and 98 cm. of this experiment, he found that if E represent the number of ions produced in certain arbitrary units by light of intensity I on unit area of

* Phil. Mag. xiv. p. 297 (1907).

plate, then using a spark between aluminium terminals,

$$\text{For distance } 37.6, \frac{E}{I} = 1.82,$$

$$\text{For distance } 110.2, \frac{E}{I} = 1;$$

and for iron terminals,

$$\text{For distance } 37.6, \frac{E}{I} = 1.78,$$

$$\text{For distance } 110.2, \frac{E}{I} = 1.$$

The difference in the two cases is due to the fact that the spectrum of the light emitted by the aluminium is different from that of the iron. But in both cases it is apparent that if the intensity is decreased by the factor $\left(\frac{37.6}{110.2}\right)^2$, i. e. $\frac{1}{9}$ about, there is a very large decrease (45 per cent.) in the ionizing power. With the Röntgen rays, even taking the isolated readings which give the extreme values and taking the rays to diverge from the anode, a decrease of $\frac{1}{16}$ only produces a change of 13 per cent.

If then the forces in a Röntgen ray pulse are in any way comparable to those in a beam of ultra-violet light, the results of this experiment discredit to some extent the pulse theory; while establishing, as they appear to do, the uniformity of the ionization per cm. in a beam of rays, they remove a possible objection to the corpuscular theory.

This research was conducted in the Electrical Laboratory at Oxford, and I should like to express my thanks to Professor Townsend for much assistance and encouragement.

X. The Positive Thermions from the Salts of the Alkaline Earths. By CLINTON J. DAVISSON, B.S., Fellow in Physics, Princeton University, Princeton, N.J., U.S.A.*

Introduction.

THAT positive electrical charge is emitted by many chemical compounds when sufficiently heated was discovered by J. C. Beattie† in 1899. Since then numerous experiments have been made to determine the laws of this

* Communicated by Prof. O. W. Richardson.

† Phil. Mag. July 1899.

emission, and the nature of the particles carrying the charge *. Experiments with the first of these ends in view have been productive of several more or less general empirical laws. Attempts to determine the nature of the ions have, however, been less uniformly successful if one may judge by the variety of answers the query has received. This lack of unanimity has arisen, it appears, from the impossibility of inferring the nature of the ions from data that can yield with certainty only the laws of emission. The small value of such data as a means of identifying the ions has been often recognized, and it has been frequently suggested that their true nature would not be known with any degree of certainty until reliable determinations of their specific charge had been made.

Of the experiments which have been made to determine the value of e/m for these ions, those of Richardson (*l. c.*) alone seem sufficiently reliable and extensive to serve as a basis for legitimate inference †. Richardson made determinations of e/m for the positive thermions from various salts of the alkali metals, and found that they admit of classification under two heads: 1st those which agree with the value of e/m for sodium or for potassium in electrolysis; and 2nd, those which agree with the electrolytic value of e/m for the metallic ions of the salt under test. From these results he has inferred that the ions which are emitted by such salts when heated are single atoms of the metal minus single electronic charges. The values of e/m corresponding to ions of sodium and potassium are taken to indicate the presence of these elements as impurities in the specimens of the salts examined.

Object.

The present investigation was undertaken for the purpose of making similar tests upon a large number of salts other

* Beattie, *Phil. Mag.* April 1901. Garrett & Willows, *Phil. Mag.* Oct. 1904. Garrett, *Phil. Mag.* June 1907. Thomson, *Camb. Phil. Soc. Proc.* 1906-1908, p. 105. Thomson, *Camb. Phil. Soc. Proc.* vol. xv. Feb. 1909. Horton, *Camb. Phil. Soc. Proc.* 1909, p. 329. Garrett, *Phil. Mag.* Oct. 1910. Richardson, *Phil. Mag.* Dec. 1910, p. 981. Richardson, *Phil. Mag.* Dec. 1910, p. 999. Horton, *Proc. Roy. Soc., A.* vol. lxxxiv. no. 572, Dec. 1910. Horton, *Camb. Phil. Soc. Proc.* vol. xvi. pt. i. Feb. 1911.

† Reliable determinations of e/m for positive ions from heated anodes coated with salts in discharge-tubes have been made by Gehrcke & Reichenheim (*Phys. Zeit.* viii. p. 724, Oct. 1907). There are good reasons for thinking, however, that such emissions in high-tension tubes are not closely related to the more strictly thermal phenomena dealt with in the present investigation.

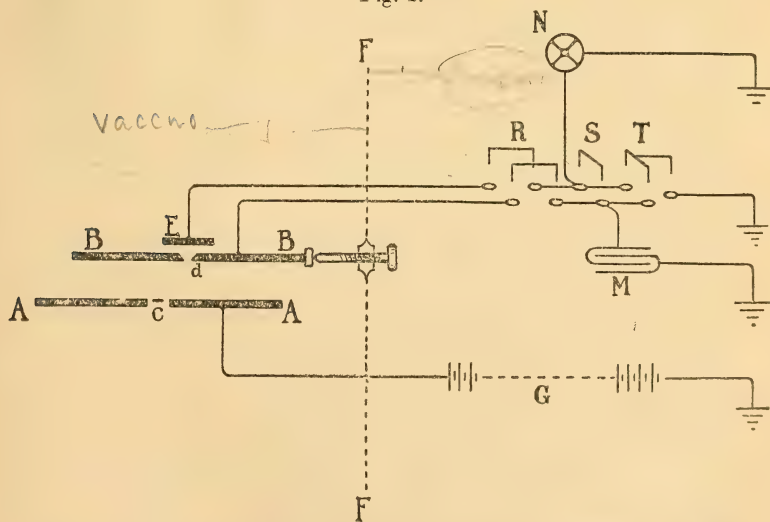
than those of the alkali metals. It seemed advisable, however, to terminate these tests temporarily with an examination of the salts of the alkaline earths and to devote a part of the available time to experiments suggested by recent investigations of Garrett and of Horton. The results of these latter experiments appear in another paper. The present paper includes an account of determinations of e/m for the positive thermions from various salts of barium, strontium, calcium, and magnesium.

Experimental Method.

The method by which these determinations have been made is that which Richardson devised for determining the specific charge of the positive thermions from different metals, and which was used by him in determining the same characteristic for the positive thermions from the salts of alkali metals in the experiments mentioned above. The rationale of this method together with a detailed description of the apparatus may be found in an article by Richardson in the *Philosophical Magazine* for Nov. 1908. It will be unnecessary in the present case, therefore, to give more than the essential features of the method and a few words concerning certain alterations in the apparatus.

In the schematic diagram (fig. 1) AA and BB represent

Fig. 1.



sections of the parts of a parallel plate condenser. A slot with its length normal to the plane of the drawing is cut in the plate AA to admit the platinum strip C. C carries on

its upper surface the salt to be examined, and is electrically heated. D designates a slit in the plate BB. D is parallel to C and approximately equal to it in width. Behind D is another plate, E, parallel to BB and insulated from it. BB and E are joined rigidly together. BB is free to move in its own plane perpendicularly to the length of D.

The parts of the apparatus to the left of the dotted line FF are *in vacuo*, but connect electrically and mechanically with the parts in air as indicated. AA and C connect to a battery of accumulators, G, which maintains them at a positive potential relative to the earth. BB and E are connected, as shown, to a system of mercury-cup switches.

If, now, positive ions are being emitted by the strip C, or by a substance on its upper surface, these will be carried across the space between AA and BB by virtue of the electric field. Most of these will reach BB, and will carry charge to it at a uniform rate, constituting a current to which we will refer as the current i_1 . A part of the ions will, however, pass through D and carry charge to E. The number of coulombs reaching E per second will be referred to as the current i_2 . The ratio of i_2 to $(i_1 + i_2)$ will depend upon the position of the slit D. From the symmetry of the apparatus it is clear that this ratio will be a maximum when D is opposite the strip. If, however, a magnetic field is established parallel to the strip in the space between AA and BB the symmetry will be destroyed; we should expect to find the maximum in $i_2/(i_1 + i_2)$ displaced in a direction depending upon the direction of the magnetic field and by an amount depending upon nearly every physical quantity involved, including the value of e/m for the ions. The way in which these physical quantities are related will be considered later. For the present we consider the method of determining $i_2/(i_1 + i_2)$.

Referring again to the system of mercury-cup switches shown in fig. 1, it will be seen that when R and T are in place the currents i_1 and i_2 will be shunted directly to earth. If T is removed the current i_1 will charge up the insulated system including BB, the condenser M, and the wires joining them, while the current i_2 will charge up the system including the plate E, the electrometer N, and their connecting wires. If, after these currents have been passing for a convenient time, say t seconds, the connexion R is removed, the parts of the two systems to the right of this connexion will have acquired potentials which will depend upon the total charges received by the two systems. These potentials will not be exactly proportional to the charges respectively,

since the coefficient of potential between the two systems is not zero. The steady deflexion acquired by the electrometer will not, therefore, be exactly proportional to $i_2 t$. When the connexion S is dropped into place the parts of the charges $i_1 t$ and $i_2 t$ to the right of R are mixed and the electrometer indicates a new potential resulting from the readjustment. This new potential is not, however, exactly proportional to $(i_1 + i_2)t$, since the fraction of this charge left on the parts of the system to the left of R is a variable depending upon the relative values of i_1 and i_2 . The ratio of the two readings of the electrometer, say θ_2/θ_1 , is not, therefore, exactly proportional to $i_2/(i_1 + i_2)$. It may be easily shown, however, that a maximum in $i_2/(i_1 + i_2)$ will be correctly indicated by a maximum in θ_2/θ_1 , and this alone is of importance in these measurements.

We shall now inquire how the displacement of this maximum by a magnetic field is related to e/m for the carriers and to the other physical quantities involved. If, in fig. 1, we choose the direction parallel to the plane AA and at right angles to the strip as the x -direction in a system of Cartesian coordinates, the direction normal to AA as the y -direction, and that parallel to the strip as the z -direction, any ion moving in the space between the two plates will satisfy the three differential equations:

$$\begin{aligned} m \frac{d^2 x}{dt^2} &= e \left\{ X + H_z \frac{dy}{dt} - H_y \frac{dz}{dt} \right\}, \\ m \frac{d^2 y}{dt^2} &= e \left\{ Y + H_x \frac{dz}{dt} - H_z \frac{dx}{dt} \right\}, \\ m \frac{d^2 z}{dt^2} &= e \left\{ Z + H_y \frac{dx}{dt} - H_x \frac{dy}{dt} \right\}, \end{aligned}$$

where X, Y, Z are the components of the electric field in electromagnetic units, and H_x , H_y , H_z are the components of the magnetic field in gausses.

The disposition of apparatus is such that

$$Y = Z = H_x = H_y = 0,$$

$$\text{and} \quad X = V/d,$$

where V is the difference of potential between AA and BB and d is the distance between them in centimetres.

Since the laws of emission of the ions from a heated surface are known, the current density at any point of the plane BB is determinate, and the calculation of $i_2/(i_1 + i_2)$ is theoretically possible. Practically, however, the problem

presents difficulties which are great compared with the usefulness of an exact solution. Richardson (*l. c.*) has given an approximate solution for the displacement of the maximum of $i_2/(i_1 + i_2)$ on the assumption that the initial velocities of the ions are small compared with the velocities which they acquire in the electric field, and on the further assumption that ions which leave the strip normally and reach the point of maximum current density when $H_z = 0$, also reach the point of maximum current density when $H_z \neq 0$. These assumptions have been tested by calculation and experiment and have been found sufficiently valid to insure values of e/m accurate to within a few per cent., which is greater than the accuracy of the measurements.

The approximate solution referred to may be written

$$x = \frac{Hd^2}{3} \sqrt{\frac{2e}{Vm}},$$

where x is the displacement of the maximum of $i_2/(i_1 + i_2)$, and H is the value of H_z .

From this we have

$$\frac{e}{m} = \frac{9}{2} \frac{Vx^2}{H^2d^4}.$$

In this expression, with the exception of x , the quantities upon which e/m depends admit of ready and fairly accurate measurement. The quantity x , which is the displacement in cms. of the maximum value of $i_2/(i_1 + i_2)$ by the magnetic field H , is measured in the following manner:—The current which heats the strip C (fig. 1) is gradually increased until the thermionic current from the salt is sufficiently large and steady for measurement. The magnetic field and electrical potential are then adjusted to appropriate values and determinations of θ_2/θ are made, as already described, with the slit in a series of different positions. The screw used in changing the position of the slit has a pitch of 0.0635 cm., and the setting can be accurately made to within less than 1/20 of a turn.

The values of θ_2/θ which represent approximately $0.041 \times i_2/(i_1 + i_2)$ are plotted against the positions of the slit and readings taken until the data indicate that the slit has passed through the maximum in $i_2/(i_1 + i_2)$. The magnetic field is then reversed and the measurements continued until the maximum has been located in its new position. Curves are drawn through the two sets of points. The distance between the two peaks indicates the value of $2x$.

Apparatus.

The apparatus employed in a few of the earlier experiments was that used by Richardson in his experiments upon the salts of the alkali metals. This apparatus was, however, designed for a different purpose, as previously mentioned, and it was soon thought advisable to replace it by another involving the same principles but better suited to the nature of these experiments. In the new apparatus all linear dimensions were increased by a factor three, and the whole so oriented that the normal to the strip pointed directly upward, as in fig. 1. These and other alterations have not been sufficiently radical, however, to call for new drawings at this time.

The magnet used with this new apparatus was one which was made in the laboratory. The pole-pieces are 7.2 cm. in diameter, and in these experiments were 3.8 cm. apart.

Experimental Results.

The experimental results which follow are classified according to the *positive* elements of the salts. Curves are included in a few cases; for the most part, however, only numerical data appear.

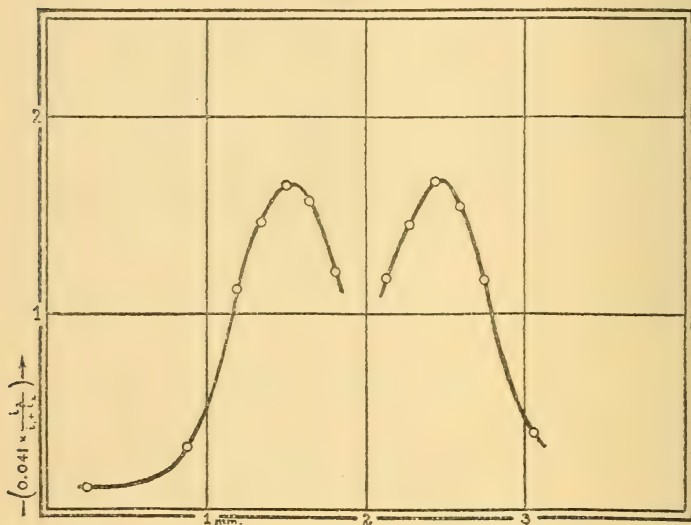
BARIUM.

The salts of barium which have been examined are the sulphate, the phosphate, the fluoride, and the chloride.

The barium sulphate used was prepared from Kahlbaum's barium chloride and Kahlbaum's ammonium sulphate. Small droplets of distilled water holding particles of the sulphate in suspension were vaporized on the upper surface of the strip, which had been previously heated to rid it of its own positive emission. After determining d , the apparatus was assembled and pumped down by means of a Gaede pump. While the evacuation was being effected the strip was heated gently to drive off what moisture might remain in the salt. When the pressure was reduced to less than 4×10^{-4} mm. of mercury by the McLeod gauge, a potential of 320 volts was established between the plates AA and BB, AA being positive to BB. On increasing the heating current gradually, a thermionic current was first noted before the strip became incandescent. This current was very transient, however, decreasing below the limit of possible measurement in a very few minutes. Similar momentary emissions were noted for

every increase of temperature up to something over 1000 C.* At this temperature the emission, though small, seemed fairly steady, and the curves shown in fig. 2 were obtained. The

Fig. 2.



magnetic field, in this case, was 2915 gausses, and the displacement of the maximum on reversing the direction of the field amounted to three turns of the screw. The complete data appear on the top line in the following tabulation:—

Barium Sulphate.

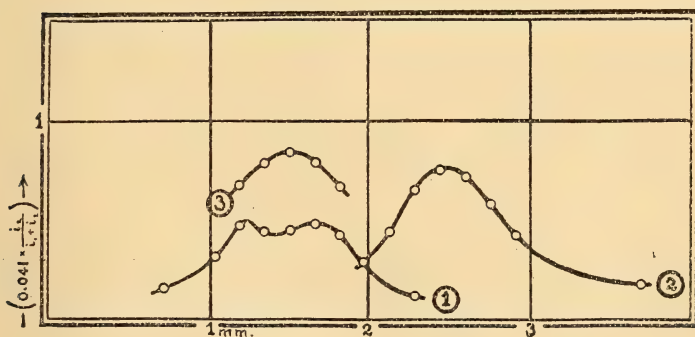
V (volts).	H (gausses).	d (cm.).	2π (cm.).	$\frac{(e/m)}{(\text{e.m. units})}$ (grams.).	$\frac{(e/m)}{\text{Ba}^{++}}$ from chemical data.
320	2915	1.275	0.190	58	142
320	2915	1.275	0.197	64	

The data on the second line are for the curves shown in fig. 3, which were obtained from the same supply of barium sulphate.

* *Note.*—The temperature of the salt, being of no great importance in these measurements, was judged from the colour of the hottest portion of the strip. In some cases comparison was made with the colour of the interior of an electric furnace whose temperature could be measured.

These values of e/m do not agree with the value of e/m for barium in electrolysis as the experiments of Richardson might lead one to expect. It will be seen, however, that the mean of the experimental values approximates to one-half the value computed from chemical data. That this approximation is not accidental, and that the large discrepancy is due to errors inherent in the experimental method, are rendered more certain by the results of experiments upon the other salts of barium, as well as those upon the salts of

Fig. 3.



the other alkaline earths. Such a relation, though unexpected, receives a ready interpretation upon the supposition that the ions are single atoms of barium minus single electronic charges, instead of such atoms minus double electronic charges as in chemical reactions.

Other curves from this supply of salt could not be obtained on account of the gradual diminution of the thermionic current.

The curves, fig. 3, exemplify an annoying type of irregularity not infrequently met with in these observations. It is evident that a decided change occurred in the distribution of emission while curves (1) and (2) were being taken, owing perhaps to a slight contortion of the strip, or to a change in the surface of the salt. In such cases curves were always taken with the magnetic field alternately in one sense and in the other until a pair of similarly shaped peaks was obtained. It is probable, however, that these time variations were always operative to some extent, and that to them are due, in part, the irregularities to be found throughout the results.

Barium Chloride.

In experiments upon this salt small crystals of Kahlbaum's barium chloride "zur Analyse" were fused on the upper surface of the strip in air; otherwise the observations were carried out as already described. All but one of the experiments on this salt were made with the apparatus used by Richardson. The results from four different samples of the salt may be summarized as follows:—

Barium Chloride.

V.	H.	<i>d.</i>	2 <i>x.</i>	<i>e/m.</i>	(<i>e/m</i>) _{Ba++}
143	4600	·532	·076	55	142
137	4600	·532	·076	60	
129	4600	·492	·082	80	
123	4600	·502	·092	88	
123	4600	·502	·089	81	
123	4600	·502	·087	77	
208	2915	1·28	·247	63	

Mean=72

Here again the observed values of *e/m*, though varying through a great range, are distributed about the value corresponding to barium atoms carrying single charges.

The temperature required to produce a measurable current was 1000° C. or more, as in the case of the sulphate. A larger and more persistent current was, however, obtainable.

Barium Fluoride.

The samples of this salt were prepared from the barium chloride used in the experiments on that salt and Baker's analysed hydrofluoric acid.

A very high temperature, considerably over 1000° C., was required to produce a measurable current. From three different samples it was only once possible to obtain more than one pair of curves before the current, even at the highest temperature, had diminished below the limit of observation. The following results obtained from this salt are similar to those obtained from the sulphate and chloride.

Barium Fluoride.

V.	H.	<i>d.</i>	2 <i>x.</i>	<i>e/m.</i>	(<i>e/m</i>) _{Ba++}
400	2915	1·28	·173	58	142
399	2915	1·29	·173	56	
401	2915	1·285	·191	70	
401	2915	1·285	·191	70	

Mean=64

Barium Phosphate.

This salt of barium proved more refractory than any one of the others tested. The curves were never smooth and were always subject to rapid time variations. The samples employed were prepared from the same supply of barium chloride used in preparing the other salts, and Kahlbaum's ammonium phosphate. Satisfactory curves were obtained but twice, and the values of e/m from these were quite different from the values obtained from the other barium salts. The data follow :—

Barium Phosphate.

V.	H.	d.	2x.	e/m .	$(e/m)_{Ba++}$
283	2915	1.275	.438	268	142
282	2915	1.275	.413	238	

Mean = 253

These very anomalous values might be disconcerting were it not for the fact that anomalous values of about this magnitude are to be found among the results for the salts of all the alkaline earths. Taken together they point to some common impurity. Similar values were found by Richardson in his investigation of the salts of the alkali metals, and were attributed by him to the presence of potassium as an impurity. Potassium salts give rise to very large thermionic currents and alkali metals are among the commonest of impurities. The values obtained for e/m in this case agree with that for potassium, which is 249. It is assumed, therefore, until some better explanation presents itself that these and similar results are due to potassium or its salts.

Another difference between these experiments and those on the other barium salts is that measurable thermionic currents were obtained at lower temperatures. Currents were measurable at 500° or 600° C., while in all other cases a temperature of more than 1000° C. was required. This emission at comparatively low temperatures was found to be characteristic of observations leading to these anomalous results. In some cases it has been possible by continued heating to rid the salt of these impurities and to finally obtain a value of e/m characteristic of the salt. In the case of barium phosphate, however, the difficulty due to time variations seemed worse at higher temperatures, and further experiment was abandoned.

STRONTIUM.

The salts of strontium that have been tested are the same as were tested in the case of barium, and, as in the case of those salts, the values of e/m are found to approximate to one-half the value of e/m for the metallic ions, as computed from chemical data. Values of e/m corresponding to potassium are more common among the results for strontium than among those for barium.

Strontium Sulphate.

This salt was prepared from H. Trommsdorff's strontium chloride and Kahlbaum's ammonium sulphate. All usual precautions were taken in the preparation of this and other salts to avoid alkaline impurities. The experiment was carried out as in the case of barium sulphate. A steady emission was obtained at a temperature as low as 550°C . The data for observations made at this temperature are given on the top line below:—

Strontium Sulphate.

V.	H.	d .	2α .	e/m .	$(e/m)_{\text{Sr}++}$	$(e/m)_{\text{K}+}$
286	2915	1.305	0.425	230	222	249
277	2915	1.305	0.286	104		
275	2915	1.305	0.289	105		

This value of e/m is taken to indicate an emission of potassium. It may be argued, of course, that 230 agrees more nearly with the electrolytic value of e/m for strontium than that for potassium, and that the ions are atoms of strontium carrying a double charge. That such is the true explanation is rendered improbable by the fact that this would make strontium an exception to an otherwise general rule. The view that the emission was potassium is also strengthened by the fact that the temperature of emission was but 550°C . or thereabouts.

The data given on lines two and three were obtained after this same supply of strontium had been subjected to twenty-one hours of continuous heating, during which the temperature had been gradually increased from about 550°C . to 1000°C . These values of e/m agree well with the relation suggested by the results on the salts of barium.

Strontium Chloride.

The samples of this salt were from a supply furnished by Eimer and Amend. Six values of e/m were obtained from one sample during a period of forty hours' heating at temperatures between 1000°C . and 1200°C .

The tabulated results follow:—

Strontium Chloride.

V.	H.	d .	$2x$.	e/m .	$(e/m)_{\text{Sr}++}$
298	2915	1.285	.257	96	222
298	2915	1.285	.254	93	
284	2915	1.285	.257	92	
325	2915	1.285	.241	92	
324	2915	1.285	.241	92	
275	2915	1.285	.273	99	

Strontium Fluoride.

Samples of this salt were prepared from Kahlbaum's strontium carbonate, Baker's analysed hydrochloric acid, and Baker's analysed hydrofluoric acid.

The results seem in no way exceptional. A measurable current was obtained at about 500°C . or 600°C . The data for this emission appear on the first line below, and are taken to indicate potassium. The data given on the second line were obtained after two hours' heating and at a slightly higher temperature.

Strontium Fluoride.

V.	H.	d .	$2x$.	e/m .	$(e/m)_{\text{Sr}++}$	$(e/m)_{\text{K}+}$
407	2915	1.34	.359	215	222	249
407	2915	1.34	.362	220		
407	2915	1.34	.263	116		
407	2915	1.34	.248	103		

After an additional heating of nine hours at about 700°C . the thermionic current was practically zero, but was re-established by increasing the temperature to about 1000°C . Two pairs of curves taken at this temperature furnished the results given on the third and fourth lines. The value of e/m for the ions at this temperature, it will be seen, agree well with one-half the electrolytic value for strontium.

Strontium Phosphate.

The emission from strontium phosphate was found to be similar to that from the corresponding salt of barium. The specimen examined was prepared from strontium nitrate of "tested purity" supplied by Eimer and Amend, and Kahlbaum's ammonium phosphate. The ammonium phosphate was the same as that used in the preparation of barium phosphate; it seems probable that this was the source of the impurity. The following data were obtained:—

Strontium Phosphate.

V.	H.	<i>d.</i>	<i>2x.</i>	<i>e/m.</i>	$(e/m)_{Sr++}$	$(e/m)_{K+}$
207	2915	1.32	.533	287	222	249
207	2915	1.32	.540	284		
401	2915	1.32	.381	281		
400	2960	1.32	.381	276		
400	2915	1.32	.381	281		

After making these determinations, what remained of the phosphate was removed from the strip with nitric acid and distilled water. Before using the strip for any other salt the apparatus was reassembled and the cleaned strip subjected to a preliminary heating to reduce its own emission again to zero. As was usually found in such cases, a measurable though short-lived current was easily obtained. A determination of e/m at the lowest temperature giving a measurable emission yielded 264, which was taken to indicate potassium. After this initial emission had disappeared the temperature of the strip was increased and additional determinations made with the following results:—

V.	H.	<i>d.</i>	<i>2x.</i>	<i>e/m.</i>	$(e/m)_{Sr++}$
394	2915	1.32	.244	108	222
418	2915	1.32	.260	131	
418	2915	1.32	.267	138	

Though great reliance may not be put upon these results, their agreement with half the electrolytic value for strontium suggests that the emission may have been due to strontium phosphate or to strontium nitrate which remained on the strip after the cleaning.

CALCIUM.

The salts of calcium which have been tested are the sulphate, the chloride, and the phosphate. The difficulty with calcium is that half the electrolytic value of e/m lies so near the value of e/m for potassium that it is not possible by the method of this experiment to distinguish between them. It is of interest, however, that out of thirteen determinations all but one may be explained on either hypothesis. This fact is also of importance as it shows what could not be shown in the case of strontium, that none of the ions are atoms of the metal carrying double charges as in electrolysis. The one exception corresponds very nearly to sodium and may very likely be due to that element as an impurity.

Calcium Sulphate.

Calcium sulphate was prepared from Baker's analysed calcium chloride and Kahilbaum's ammonium sulphate.

Momentary currents were noted for temperatures between 500° C. and 1000° C., but no steady emission was obtained below the latter. Very good curves were obtained, however, at and above this temperature. The corresponding data appear in the first three lines below.

Calcium Sulphate.

V.	H.	d .	$2x$.	e/m .	$(e/m)_{Ca++}$	$(e/m)_{K+}$
409	2915	1.29	.343	230	487	249
407	2915	1.29	.349	236		
432	2915	1.29	.327	220		
150	4600	0.50	.105	258		
150	4600	0.50	.095	215		
150	4600	0.50	.105	258		

The data and results occurring in the remainder of the Table are from previous experiments with the apparatus used by Richardson. In these experiments the same high temperature was required to obtain a measurable emission as in those already mentioned. The observed values of e/m point to either potassium or calcium carrying single charges, while the temperature of emission argues more strongly in favour of the latter.

Calcium Chloride.

Although a great number of experiments have been made to obtain results from this salt, satisfactory curves have been obtained in but two cases. The samples under investigation

were from a supply of Baker's analysed calcium chloride. Various methods of coating the chloride on to the strip were tried, but without apparent effect upon the irregularity of the emission. In the successful experiments mentioned the values of e/m were found to be 380 and 276. Although these approximate to the electrolytic value for calcium and one-half that value respectively, it seems more probable that they are due to emissions of sodium and potassium; the approximations are better, and the temperatures at which the curves were obtained were much below 1000°C . The data occur on the first two lines in the following table:—

Calcium Chloride.

V.	H.	d .	$2x$.	e/m .	$(e/m)_{\text{Ca}++}$	$(e/m)_{\text{K}+}$	$(e/m)_{\text{Na}+}$
148	4600	0.48	.161	380	487	249	422
148	4600	0.48	.136	276			
147	4600	0.49	.140	264			

The data on the bottom line are for a mixture of calcium chloride and calcium sulphate. The temperature in this case was high and the emission may have been calcium.

Calcium Phosphate.

This salt was prepared from Baker & Co's. analysed calcium chloride and Kahlbaum's ammonium phosphate. The observed values of e/m approximate to one-half the electrolytic value for calcium, but judging from the cases of barium phosphate and strontium phosphate prepared from the same supply of ammonium phosphate, it seems probable that the emission was really due to potassium. The results follow:—

Calcium Phosphate.

V.	H.	d .	$2x$.	e/m .	$(e/m)_{\text{Ca}++}$	$(e/m)_{\text{K}+}$
206	2915	1.32	.555	271	487	249
402	2915	1.32	.331	249		
401	2915	1.32	.359	220		
400	2915	1.32	.375	240		

MAGNESIUM.

The salts of magnesium tested have been the chloride, the fluoride, and the phosphate. It seems probable from the variation of the values of e/m with the temperature that a

true emission of magnesium atoms carrying single charges was obtained from both the chloride and the phosphate.

Magnesium Chloride.

The samples of this salt tested were from a supply of Kahlbaum's magnesium chloride "zur Analyse." Measurable currents were obtained at comparatively low temperatures. The curves were erratic at these temperatures but improved at the higher ones. The data and results follow:—

Magnesium Chloride.

V.	H.	<i>d.</i>	2 <i>x.</i>	<i>e/m.</i>	(<i>e/m</i>) _{Mg++}	(<i>e/m</i>) _{K+}
408	2915	1·305	·343	218	800	249
408	2400	1·305	·302	247		
407	2400	1·305	·317	320		
407	2400	1·305	·397	428		
407	2400	1·305	·397	428		

The first values are probably due to potassium. The final ones, which are for a temperature of about 1100° C., are taken to indicate magnesium atoms carrying single charges.

Magnesium Phosphate.

The curves for magnesium phosphate were better, on the whole, than for any of the phosphates already mentioned. During twenty-four hours' heating the values of *e/m* fluctuated between the value for potassium and that for magnesium. The value obtained at the highest temperature corresponded most nearly to the value for magnesium. In the following Table the data and results occur in order of increasing temperature. The final value is for a temperature of from 1100° C. to 1200° C.

Magnesium Phosphate.

V.	H.	<i>d.</i>	2 <i>x.</i>	<i>e/m.</i>	(<i>e/m</i>) _{Mg++}	(<i>e/m</i>) _{K+}
400	2400	1·285	·311	279	800	249
395	2400	1·285	·321	291		
395	2400	1·285	·359	365		
395	2400	1·285	·343	333		
395	2400	1·285	·355	358		
395	2400	1·285	·355	358		
395	2400	1·285	·387	423		
395	2400	1·285	·387	423		

Magnesium Fluoride.

The curves for this salt were always irregular and variable, but one pair of reliable curves was obtained, and that gave a value of *e/m* corresponding to potassium.

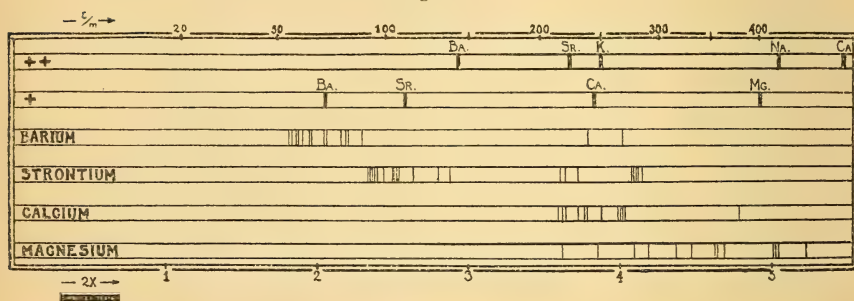
Magnesium Fluoride.

V.	H.	d .	$2x$.	e/m .	$(e/m)_{Mg^{++}}$	$(e/m)_{K^+}$
402	2400	1.23	.286	258	800	249

COLLECTED RESULTS.

In fig. 4 the results of all these experiments are gathered together and exhibited graphically. The scale at the bottom

Fig. 4.



of the figure represents values of $2x$, while that at the top gives the corresponding values of e/m subject to the conditions that $V = 350$ volts, that $H = 2900$ gauss, and that $d = 1.3$ cm., which are taken to be approximately the mean values of these quantities. In the space labelled "++" the heavy vertical marks designated "Ba," "Sr," &c. are placed beneath the values of e/m for these elements as calculated from chemical data. The corresponding readings on the lower scale therefore indicate the distances by which the peaks of the experimental curves would be separated provided the emission were that of the ions in electrolysis, and provided V , H , and d had the values already mentioned. In the next space the values of $2x$ in like manner correspond to atoms of "Ba," "Sr," &c., carrying single charges. In the space labelled "Barium" the vertical marks correspond to the experimental values of e/m from all the salts of barium examined. The results for the other salts are exhibited in the remaining spaces. The length of the heavy black mark in the lower left-hand corner of the figure represents the width of the slit on the scale of $2x$.

Exhibited in this manner the results of these experiments point strongly to the conclusion that the truly characteristic positive thermions from salts of alkaline earths are single atoms of these elements minus single electronic charges.

My very best thanks are due to Prof. O. W. Richardson for suggesting this investigation and for advice throughout the whole of it. I also wish to thank Mr. C. Bol for care exercised in constructing the glass parts of the apparatus, and Mr. E. Keil and Mr. W. Duryea for their careful construction of the metal parts.

APPENDIX.

Since the completion of the experiments described above a series of determinations has been made of the specific charge of the positive thermions from zinc sulphate. Of several salts of zinc tested the sulphate alone gave reliable curves. The results of the measurements on this salt appear to confirm the rule which has been found so far to be general, that the positive thermions are single atoms of the metal of the salt minus single electronic charges. The data follow:—

Zinc Sulphate.

V.	H.	<i>d</i> .	<i>2x</i> .	<i>e/m</i> .	(<i>e/m</i>) _{Zn(+ +)}	(<i>e/m</i>) _{Zn(+)}
282	2915	1.295	.368	179	297	148
282	2915	1.295	.368	179		
282	2915	1.295	.375	186		
481	2915	1.295	.263	157		

XI. *The Rôle Played by Gases in the Emission of Positive Thermions from Salts.* By CLINTON J. DAVISSON, B.S., Fellow in Physics, Princeton University, Princeton, N.J., U.S.A.*

IN the preceding paper the author has adduced experimental results which show that the positive thermions from salts of the alkaline earths in air at pressures under 10^{-4} mm. of mercury are—excepting those that apparently arise from impurities—single atoms of the metals of such salts minus single electronic charges. This result, it has been pointed out, is in accord with that obtained by Richardson in similar experiments upon the positive thermions from salts of the alkali metals. Although, from the nature of the experimental method and from the results, there can be little doubt as to the validity of the main conclusions arrived at in these investigations, it may not be said that they dispose of all other hypotheses which have been entertained up to the present time regarding the nature of this class of ions. It may not be said, for

* Communicated by Prof. O. W. Richardson.

example, that these results contain any direct evidence against the hypothesis that, in some cases, all or a part of the thermionic current is carried by carbon monoxide. Horton* found that in the case of a sample of aluminium phosphate which he investigated, the electrical emission was accompanied by an emission of carbon monoxide, from which he has inferred that the carbon monoxide was carrying the current. Neither is it legitimate from these results, which are for very low gas pressures, to conclude that no part of the current is carried by atoms or molecules of the gas in contact with the salt. Garrett† and also Horton‡ found that at constant temperature the electrical emission depends in a very marked way upon the pressure and nature of this gas. Garrett concluded from the nature of this dependence that heated salts emit neutral doublets which are split apart by collision with gas molecules. Horton (*l. c.*) has raised what appear to be valid objections to this hypothesis and has concluded that the gas atoms or molecules take an active part in the transfer of charge.

The present paper includes an account of various experiments which have been carried out for the purpose of testing these special hypotheses by determinations of the specific charge of the thermions from salts under conditions similar to those obtaining in the experiments of Garrett and of Horton.

The method by which these determinations have been made is identical with that described in the paper above on "Positive Thermions from Salts of Alkaline Earths."

The relation between the electrical and gas emissions was taken up in connexion with the experiments on strontium chloride described in the paper mentioned above. It was noticed during these experiments that the gas pressure in the apparatus was higher when the strip was heated than when it was not. In a case investigated the pressure in the apparatus when the strip was not heated was 7.6×10^{-5} mm. by the McLeod gauge. With the strip at a temperature of approximately 1000° C. the pressure increased and became uniform at 99×10^{-5} mm. The Gaede pump in connexion with the apparatus was running continuously.

In order to determine, if possible, the nature of this gas the pumping was discontinued while the strip was being heated and the evolved gas allowed to accumulate. After ten or fifteen minutes the part of the gas in the bulb of the McLeod gauge was compressed into the capillary and

* Proc. Roy. Soc. A, vol. lxxxiv, no. 572, Dec. 1910.

† Phil. Mag. Oct. 1910.

‡ Camb. Phil. Soc. Proc. vol. xvi, part i, Feb. 1911.

examined spectroscopically. An electrodeless discharge was established through the gas between strips of lead foil which encircled the capillary at points four or five centimetres apart. An induction-coil was employed in exciting the discharge, and the wave-lengths of the emitted light were determined by means of a Hilger direct-reading spectrometer. The lines observed appear in the left-hand column of the following table :—

Lines observed.	Hg *.	CO †.	Lines observed.	Hg *.	CO †.
	615		519		519
606		607		495	
579	578		482		483
568	568		450		450
560	559	560	435	436	
546	545				

* Watts.

† Hagenbach & Konen.

Comparing these wave-lengths with those given in the second and third columns it is evident that at least a part of the evolved gas was carbon monoxide, as in Horton's experiments, or carbon dioxide, since this gas splits up in a discharge-tube and gives the carbon monoxide spectrum.

The apparatus was not, in the present case, free from grease and other possible sources of organic matter, and it was, therefore, necessary in order to determine if the carbon monoxide came actually from the salt to carry out a blank experiment. For this purpose the strontium chloride was removed from the strip by means of distilled water and the experiment repeated. The evolution of gas was at first as large as before. After a short time, however, the difference in pressure when the strip was heated and when it was not began to decrease, and finally became immeasurably small.

Before running this blank experiment, and while the strontium chloride was apparently evolving considerable quantities of carbon monoxide, several determinations were made of the specific charge of the ions. The observed values, although somewhat low, are taken to indicate an emission of strontium atoms minus single electronic charges. Five determinations gave the values 96, 93, 91, 92, and 92. One-half the electrolytic value of e/m for strontium is 111, while the values of e/m for carbon monoxide and carbon dioxide molecules carrying single positive charges are 348 and 243 respectively. It seems evident, therefore, that although the

electrical emission was, in all these cases, accompanied by the emission of carbon monoxide or carbon dioxide, the gas molecules did not carry the current.

One other point was tested before running the blank experiment mentioned above. It was thought desirable to determine if any quantitative relation existed between the electrical and gas emissions. The results of two experiments with this end in view are tabulated below. In Table I. the temperature of the strip was adjusted to about 1000°C . at three o'clock. The subsequent observations show that although the gas pressure had reached an equilibrium in fifteen minutes the electrical emission was still increasing at the end of forty minutes.

TABLE I.

Time.	Thermionic Current in Amperes.	Equilibrium Pressure in mm. of Hg.
3 00	0	5×10^{-5}
3 15	8.4×10^{-12}	129×10^{-5}
3 22	12.0×10^{-12}	122×10^{-5}
3 30	24.0×10^{-12}	129×10^{-5}
3 40	48.0×10^{-12}	129×10^{-5}

The experiment was necessarily discontinued at this point. The heating current was reduced to zero, but the pumping continued. Five hours later the temperature of the strip was again adjusted to about 1000°C . and observations continued over a period of twenty-four hours. These observations, which appear in Table II., are strongly in support of the view that the two emissions are entirely independent. Similar results were obtained by Richardson * in an investigation of the relation between gas emission and the emission of positive thermions from platinum. A determination of e/m made after 10 00 A.M. (see Table II.) gave the value 100, which compares favourably with one-half the electrolytic value for strontium, 111.

Experiments similar to these have also been made upon a sample of strontium sulphate with essentially the same results. A slight increase in the gas pressure was noted when the strip was heated to about 600°C . A determination of e/m at this temperature indicated potassium, the value

* Congrès de Radiologie, *Comptes Rendus*, Brussels, 1905.

TABLE II.

Time.	Thermionic Current in Amperes.	Equilibrium Pressure in mm. of Hg.
8 33 P.M.	0	5×10^{-5}
8 34	0	38×10^{-5}
8 37	0	68×10^{-5}
8 42	0	91×10^{-5}
8 46	$< 5 \times 10^{-12}$	99×10^{-5}
8 54	$< 5 \times 10^{-12}$	99×10^{-5}
9 11	$< 5 \times 10^{-12}$	114×10^{-5}
9 23	$< 5 \times 10^{-12}$	129×10^{-5}
10 10	$< 5 \times 10^{-12}$	121×10^{-5}
<i>Heating and pumping continued overnight.</i>		
9 00 A.M.	48×10^{-12}	91×10^{-5}
10 00	48×10^{-12}	99×10^{-5}
2 30 P.M.	38×10^{-12}	76×10^{-5}
8 00	$< 5 \times 10^{-12}$	84×10^{-5}

being 230. At something over 1000° C. the equilibrium pressure was a little higher than any noted in the experiment on strontium chloride. A spectroscopic examination of the gas indicated mercury vapour and carbon monoxide as in the former case. Determination of e/m at this temperature gave 104 and 105 which are in agreement with 111, one-half the electrolytic value for strontium.

Taken together these results constitute a strong argument against the hypothesis that any part of the positive thermionic current from a heated salt is carried by carbon monoxide.

Another series of experiments has been made to determine the rôle played by the gas in contact with a surface of heated salt. In particular to determine if the increase in thermionic current at constant temperature which Garrett (*l. c.*) and Horton (*l. c.*) have shown to be brought about by an increase of gas pressure up to one or two millimetres is, in fact, due to an absorption of atoms or molecules of the gas and their re-emission in a charged condition.

For this purpose it was proposed to study the behaviour of the curves for some salt as the gas pressure in the apparatus was gradually increased. It was desirable, of course, to choose a salt which should give a large steady

emission at not too high a temperature, and one for which the curves should be, at the same time, as free as possible from time variations. These requirements were found to be met most satisfactorily by a sample of aluminium phosphate. The only unfortunate thing about this particular sample was that the large emission seemed not to be characteristic of the salt itself, but to arise from sodium which was present as an impurity. Only after the salt had been heated for hours together did the value of e/m indicate an emission of aluminium ions, and then only at temperatures in the neighbourhood of 1200°C .

That the large emission was, in fact, due to sodium was made more certain by an examination of the flame spectrum of aluminium phosphate from the same supply. A Gouy sprayer was partly filled with distilled water, and the spray from this forced into a Bunsen flame in the usual way. The spectroscope under these circumstances revealed only an occasional faint flash of sodium. On adding a small quantity of the aluminium phosphate to the distilled water the D lines immediately shone forth.

The first measurable emission from this aluminium phosphate occurred at about 550°C . The curves were very good and gave with the other data 254 as the value of e/m . This was taken to indicate potassium, 249. The salt was then heated continuously at this temperature for twenty-one hours. After this heating curves were taken at 600°C . which seemed to indicate sodium, the value of e/m being 439, compared with sodium 421. That the potassium value did not persist in this case, as in the case of the other phosphates tested, does not seem unreasonable. The aluminium phosphate was from a supply furnished by Kahlbaum, while the others were prepared in the laboratory from a common supply of ammonium phosphate. Further determinations of e/m during the next forty hours indicated that the emission was homogeneous, beautifully regular, and altogether suitable for the proposed tests.

The gases which have been tested are air, hydrogen, and carbon dioxide. In each case the apparatus was first thoroughly washed out with the gas to be investigated and the pressure then reduced to the lowest attainable. The gases were in all cases carefully dried. A pair of curves was taken at this low pressure. A small quantity of dried gas was admitted to the apparatus. The pressure was recorded and curves again taken. This was repeated until further measurements were impossible.

The results for these experiments for air are graphically

exhibited by the curves, fig. 1. It will be seen that the first effect of increasing the pressure is a slight scattering of the

Fig. 1.

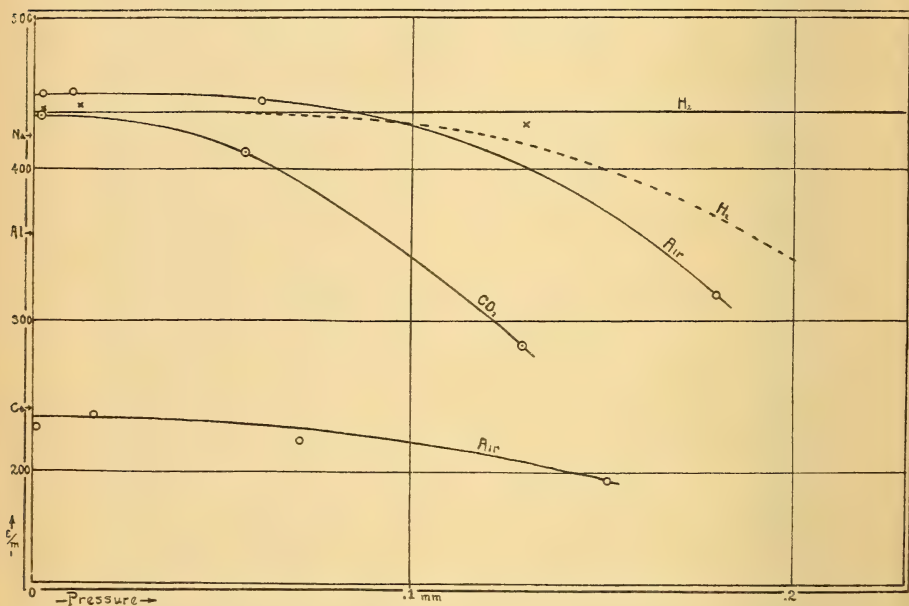


ions by collision which results in a lowering and broadening of the curves. As the pressure is further increased this lowering and broadening becomes more marked. Before the curves are completely flattened out the gas also begins exerting an appreciable effect upon the value of $2x$, the distance between the peaks. The gas interferes with the

magnetic deflexion of the ions and the maxima draw nearer together. This, of course, causes an apparent decrease in the value of e/m .

The effects produced by hydrogen and carbon dioxide were found to be similar to those produced by air, except that, as was to be expected on account of the differences in molecular weights, hydrogen produced a smaller effect, at a given pressure, than air, while carbon dioxide produced a greater. This relation is clearly exhibited by the curves, fig. 2, which

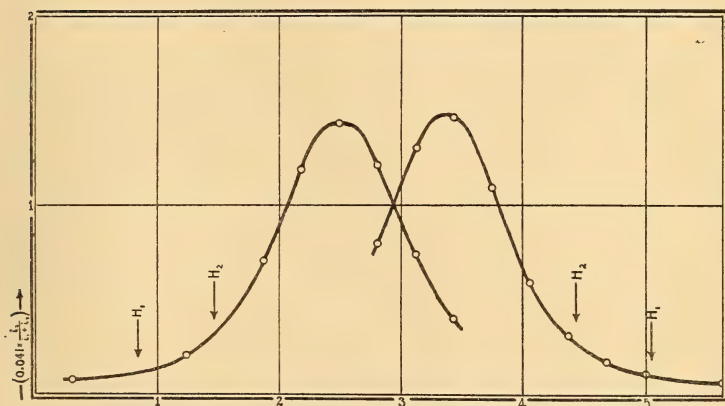
Fig. 2.



coordinate apparent values of e/m and pressures for the different gases investigated. The curves near the top of the figure are for the emission from the sample of aluminium phosphate. The scale of pressures is in millimetres, as indicated, except in the case of the dotted curve marked " H_2 " for which the scale of pressures is in centimetres. The single curve near the bottom of the figure is for a sample of calcium sulphate which was used in a preliminary experiment. It is interesting to note that in this case the apparent decrease in the value of e/m is less for a given air pressure than in the case of the sodium emission from aluminium phosphate. This, of course, is what one would expect on account of the difference in mass of the ions.

It is known from the experiments of Garrett and of Horton that the highest pressures in the present experiments cause marked increases in the thermionic emission. In no case, however, does the value of e/m suggest that gas molecules are participating in the transfer of charge. If secondary maxima due to oxygen, nitrogen, carbon monoxide, or carbon dioxide existed they would have appeared in these curves. To settle this point for the case of hydrogen curves were taken in this gas at a pressure of about one millimetre and with a reduced magnetic field. The arrows (fig. 3) indicate the positions at

Fig. 3.



which maxima due to atomic and molecular hydrogen would appear on these curves if any appreciable part of the current were carried by such atoms or molecules.

Conclusions.

1. The carbon monoxide or carbon dioxide which is sometimes emitted by samples of salts when heated is uncharged.
2. The increase of thermionic emission from a salt which is caused by the presence of a gas in contact with its surface is not due to an emission of gas atoms or molecules which have been absorbed by the salt and are emitted in a charged condition.

My sincere thanks are due to Prof. O. W. Richardson for much valuable advice throughout these investigations.

XII. *Effect of Electricity on Streams of Water Drops.* By
E. F. BURTON, B.A., *Associate Professor of Physics, University of Toronto,* and W. B. WIEGAND *.

[Plate VI.]

RECENT developments in Physics and Physiology have accentuated the importance of the part played by surface-tension in natural phenomena, and consequently led to examination of the causes which appear to affect materially the value of the surface-tension between two given media. In particular, the study of colloidal solutions has brought into prominence the inter-relation of surface-tension and electrification.

The purpose of the experiments outlined in the following paper was to examine the nature and causes of the well-known effect of bringing a charged body into the neighbourhood of the spray of water issuing in a nearly vertical line from a small nozzle. If a stream of water be directed vertically to a distance of even several feet and then allowed to fall on a sheet of metal, one recognizes the sound of the falling water as that of small falling drops; however, if a charged body such as an ebonite paddle be brought gradually near to the stream just at the point where it begins to break into drops after issuing from the nozzle, the sound of the falling water is unmistakably that due to much larger drops than before. As has been already pointed out by Lord Rayleigh †, the falling water in the second case if caught in an insulated dish will be found to be charged, a phenomenon analogous to the Kelvin water-dropper.

From time to time Rayleigh ‡ has reported the results of many beautiful experiments on this and the allied phenomena of water-jets. Photographs (Pl. VI. figs. 1 & 2), taken instantaneously by the writers, represent well what happens in the stream when the charged body is approached; they are quite similar to the photographs published some years ago by Rayleigh. The stream was directed in a nearly vertical line from a nozzle of glass, the opening of which was a circle of a few millimetres diameter. Attention may be directed to the following characteristics of these streams, which have been illustrated time and again in photographs taken during the progress of these experiments:—

* Communicated by Prof. J. C. McLennan.

† Sc. Papers, i. p. 372, § 59.

‡ Sc. Papers, vols. i. to iv.

(1) No perceptible difference in the appearance of the streams as they break into drops is betrayed.

(2) In each stream there is very apparent non-uniformity in the size of the drops in the stream; this is perhaps to be expected on account of the disturbing influences due to the velocity of the stream and the random vibrations in the air at the point of breaking into drops.

(3) One striking difference between the jets—a difference much more accentuated in photographs which follow—is the alignment of the drops of the charged stream as they proceed to the summit, and the scattering of the uncharged drops. This is of course in apparent contradiction to the repulsive action one might expect from the fact that the drops in the charged stream are all charged with electricity of the same sign.

(4) As a consequence of the phenomenon in (3) the charged drops coalesce at the top of the stream into large non-uniformly sized drops; the coalescence takes place at the portion of the stream where the velocities have become small and consequently when, as Rayleigh points out, the water in the stream collects into smaller total volume on account of the continuity of the flow.

Photographs such as those above reveal, however, only half truths; they represent the effect in the charged streams under only feeble electrifications. When the stream was influenced by charges at the potentials as high as those given by electrical machines or induction-coils, Rayleigh found that the stream indicated strong repulsion between the drops.

Rayleigh ascribes the whole action in both streams to collisions. In the uncharged stream the drops rebound after collision, and we have the consequent scattering; while in the charged stream the electrification in some way leads to coalescence. His words are as follows* :—

“As the liquid masses approach one another the intervening air has to be squeezed out. In the earlier stages of approximation the obstacle thus arising may not be important; but when the thickness of the layer of air is reduced to the point at which the colours of thin plates are visible, the approximation must be sensibly resisted by the viscosity of the air which still remains to be got rid of. No change in the capillary conditions can arise until the interval is reduced to a small fraction of a wave-length of light. But such a reduction, unless extremely local, is strongly opposed by the remaining air. It is of course true that this opposition is temporary. The question is

* Sc. Papers, iv. p. 415, § 251.

whether the air can be anywhere squeezed out during the short time over which the collision extends.

“It would seem that the electrical forces act with peculiar advantage. If we suppose that upon the whole the air cannot be removed, so that the mean distance between the opposed surfaces remains constant, the electric attractions tend to produce an instability whereby the smaller intervals are diminished while the larger are increased. Extremely local contacts of the liquids, while opposed by capillary tension which tends to keep the surfaces flat, are thus favoured by the electrical forces, which moreover at the small distances in question act with exaggerated power.”

From our study of the phenomena of such streams we are convinced that this explanation is at most merely a first approximation to the whole action. The part that surface tension can play is limited in the way noted above by Rayleigh. The identical appearance of the charged and uncharged streams, just after breaking into drops, shows that surface-tension is not altered in a way which would give rise to larger drops at breaking. It has been pointed out by Merritt and Barnett * that the apparent diminution of the surface-tension when, for example, soap-bubbles, globules of mercury, &c., are electrified, is probably due to the fact that the surfaces employed are convex, and that “in the case of a concave charged surface a consideration of the electrostatic forces would lead us to expect an apparent increase in the strength of the surface film.” If the electrostatic forces be allowed for in these cases, these writers find no perceptible direct variation in the surface-tension of a charged water or mercury surface. Such a problem as we are discussing here is of course independent of the phenomena involved in the capillary electrometer (see Barnett) †. Even treating the effect of the electrostatic forces as a diminution in the surface-tension, the experiments of Nichols and Clark ‡ show that for the low voltages employed in these drop experiments such diminution would be itself imperceptible. The effect must depend then directly on the electrostatic attractions and repulsions between the drops themselves.

Purpose of the Experiments.

The purpose of the following experiments was (1) to examine a given stream under influence of charges induced

* Phys. Rev. x. 1900, p. 65.

† Phys. Rev. vi. 1898, p. 257.

‡ Phys. Rev. iv. 1897, p. 375.

by known voltages, which were gradually increased so as to have at will either the phenomenon of coalescence or scattering referred to by Rayleigh ; (2) to photograph the streams instantaneously so as to obtain the relation between the sizes of the drops in the charged and uncharged streams; (3) to find the reason for the coalescence of the charged drops for small electrifications.

Apparatus.

For the remaining photographs the streams were shot under constant pressure in directions nearly vertical from a nozzle of glass, the circular opening of which was $\cdot 018$ cm. Under the pressure used the fine stream rose to a height of about 15 cm. It was found that the scattering at high voltages took place in larger streams, such as used in figs. 1 and 2, only at the potential of some thousands of volts obtainable from an ordinary electrical machine. However, with the smaller stream the whole range of phenomena was available by using some 700 or 800 volts from a series of small storage-cells. The glass nozzle was supported in the axis of a short vertical cylinder of brass, 5 cm. in diameter and 3.2 cm. long ; the stream broke into drops about the centre of the upper end of the cylinder. By charging the brass ring to any voltage a charge is induced on the drops as they break from the main earth-connected stream of water issuing from the nozzle. Other things being equal, the charge induced on the drops depends merely on the potential of the inductor, so that even with a piece of ebonite or glass rubbed very slightly the potential of these inductors, and consequently the charge induced on the drops, may be very large.

A focal-plane shutter was used for instantaneous exposure rather than the spark from an induction-coil and leyden-jars, in order to have the stream absolutely free from all electrical influence except that of the charging ring. In addition to the necessity for very carefully screening off all electrical discharges, the electrical illumination does not offer the same ease of manipulation. For observation with the eye the shadow of the stream cast by an arc lantern was focussed by means of a good camera lens on a sheet, and the drops viewed by means of a stroboscopic disk. In this way many observations could be made with the eye and instantaneous photographs taken of typical cases.

Results.

The photographs figs. 3 to 7 (Pl. VI.), taken with an exposure of one-fifth of a second, will give an idea of the general phenomena observed as the potential of the brass ring, visible in the photograph, was successively zero (figs. 3 & 4), +160 volts (fig. 5), +240 volts (fig. 6), and +720 volts (fig. 7). For low potentials up to about 20 volts the stream varied little from that of figs. 3 & 4, while as the voltage was increased the form shown in fig. 5 was reached at about +80 volts. The appearance was unchanged for increasing voltages up to 160, and then it changed gradually, took the form of fig. 6 at 240 volts; the spreading became more pronounced (fig. 7) as the voltages were further increased up to 700 or 800 volts and beyond. In case of each of figs. 4, 5, and 6 the stream was directed very slightly out of the vertical; for figs. 3 and 7 the stream was approximately vertical. In the cases of figs. 4 and 5 the descending spray was intercepted by an earth-connected metal plate, in order to give an uninterrupted view of the ascending stream. The details of pressure of water, size of nozzle, position of nozzle with respect to inductor-ring, &c., were constant for all these photographs.

The following characteristics of the main stream in these cases should be remarked:—(1) The natural uncharged stream begins to scatter almost as soon as the drops are formed; on the original photographs the spraying of the stream can be noticed almost immediately above the then earth-connected brass ring; (2) with each of the charged streams there is undoubted alignment of the drops making up the stream. As later photographs will show, this cannot be attributed to coalescence of the small drops on collision, for instantaneous photographs show large and small drops absolutely aligned in the main stream. In fig. 5 the alignment is apparent to the very top of the stream; in fig. 6 the scattering takes place about two thirds of the way to the top, while in fig. 7 much more violent scattering takes place much earlier in the course of the stream. The scattering in the last two cases undoubtedly is due to the repulsion between the similarly charged drops, as it increases in effect with increasing voltages. The crucial point in the explanation of the phenomena is without doubt the study of the forces bringing about the alignment of the drops long before collisions come into play.

The rest of the photographs presented may be divided into three groups, being instantaneous exposures at various parts of the streams shown in figs. 3 to 7.

(1) Figs. 8 *a*, 8 *b*, 8 *c*, from the streams just above the nozzle in the cases when the inductor was charged to zero, +80 volts, and +720 volts. The velocity of the stream was unfortunately too great to give clear cut drops in these cases, but sufficient is shown to bear out the conclusion illustrated better in figs. 1 and 2, viz., that there is no apparent difference between the sizes of drops as they break from the uncharged and charged streams. The absolute alignment of the drops in the 80 volt case may be noted, while both of the other streams give indication of instability.

(2) Figs. 9 *a*, 9 *b*, and 9 *c* show photographs of the streams higher up than the preceding. Fig. 9 *a* shows the uncharged stream (of fig. 4) just as the scattering begins; there are indications of the breaking up of the larger drops which may be due to collisions. Fig. 9 *b* shows the complete stream for the inductor charged at +80 volts (similar to the case of fig. 5). Three characteristics may be noted: (1) Variation in the size of the drops in the stream; (2) absolute alignment of the stream up to the top of its course; and (3) no indication of coalescence or collision until the top of the stream is reached, that is, until successive drops have completely gained on their neighbours preceding (the stream was directed slightly out of the vertical). When the inductor-tube was charged to +720 volts the arrangement of the drops is shown in fig. 9 *c*. The exposure was made at the point where the stream (see fig. 7) just begins to scatter. Up to the point where the scattering takes place we have the same appearance as that in 9 *b* in regard to variation in size of the drops and alignment of the stream.

(3) Figs. 10 *a* and 10 *b* are photographs of the very tops of the streams charged by the inductor at +240 volts and +720 volts respectively (see figs. 6 & 7). There is a greater proportion of small drops with the higher voltage than with the lower, from which we might conclude, keeping in mind the foregoing photographs, that there is a splitting up of the large drops at the higher voltage. Of course the higher the charge on the drops the greater the disintegrating force and, although the voltage of the drops is much below the limit set by Rayleigh* for instability, nevertheless with the motion which the particles have and the influence of the presence of other charged drops, it is conceivable that the larger drops may be split up under the influence of the electrostatic tensions over their surfaces. There also seems to be a

* Phil. Mag. [5] xiv. p. 184.

greater uniformity in the size of the drops with 720 volts, which may be explained if splitting up took place.

In each of these cases it is interesting to note that the larger drops are concentrated in the line of flow of the original stream, which would be up the centre of the photograph.

Fig. 11 is the photograph of a centimetre scale (1, 2, 3 cm.) taken with the same magnification as that employed in the photographs figs. 9 & 10, so that a rough idea of the size of the drops may be had.

Theoretical.

In striving to arrive at a coherent explanation of the phenomena observable in these experiments we may summarize the facts which appear :

1. The presence or absence of a charge on the inductor does not seem to affect perceptibly the size of the drops breaking away from the stream.

2. There is by no means uniformity in the size of the drops, large and small ones occurring at random, whether the drops are charged or not.

3. The uncharged stream almost immediately begins to scatter in all directions.

4. No matter how large the charge on the inductor-ring, *i. e.*, no matter how large the charges on the drops, there is in every case of the charged drops an absolute alignment of the drops for at least a part of their journey. For lower voltages (dependent probably on the size and velocity of the stream) there is complete alignment to the top of their course.

5. For lower voltages on the inductor-tube there is coalescence of the drops in the region of slow velocities.

6. For higher voltages the stream begins to scatter after a region of absolute alignment, and indications are given of the splitting up of larger drops into smaller in this region of scattering.

We must conclude in the first place that the breaking into drops is primarily due to the property of the surface-tension of a liquid whereby a long cylinder of liquid is unstable ; that the resulting drops are not uniform in size is due, as we may gather from Rayleigh's writings, to the irregularities induced by the rapid motion of the stream, to disturbances due to the breaking off of drops, and also to random vibrations in the air at the breaking point. Rayleigh ascribes the scattering of the uncharged stream to the

collisions between neighbouring drops. The case seems to be somewhat analogous to that of a waterfall which is partially broken up into drops as it falls, the direction of motion of the resulting drops being greatly influenced by the friction of the air and accidental vibrations or currents in the air. Fig. 1 gives evidence of collisions breaking large drops into small ones which will follow somewhat erratic courses. When collisions do occur in such a stream, the tendency to break the drops into smaller ones must be greater than any tendency towards coalescence, as capillary action will not come into play until the opposing surfaces are extremely close.

However, when we turn to the cases of the streams of charged drops, we have to deal with the extremely complicated problem of the interaction of charged spheres at various distances from one another. In these cases we have three outstanding facts, (1) the alignment of the stream of charged drops, (2) the coalescence of charged drops under certain circumstances, and (3) the scattering and possible splitting up of charged drops under other circumstances.

One suggested explanation for the alignment of the charged drops was the force exerted by the charged ring itself on a drop not on the central axis of the cylindrical inductor. The resultant value of the force of the ring on the drop will urge the drop to take a path along the axis. However, when instead of the charged ring one uses a rubbed ebonite paddle the same phenomenon is noticeable, although the force towards an axis does not exist. Again, the stream taken from an insulated bottle was charged directly by joining it up with the pole of a battery and similar results followed. That is the alignment is undoubtedly a result of the charges possessed by the drops.

Again, the alignment cannot be due to the coalescence of the drops on collision, as a comparison of figs. 4, 5, 9 *a*, 9 *b*, and 9 *c* will show. The small and large drops in the latter two cases are absolutely aligned before either coalescence or dissipation comes into question.

There remains then the outstanding problem of the interaction of two spheres charged with electricity of the same sign. Elementary consideration of the electrostatic problem tells us at once that the action is not always repulsion except in the single case of equal and similar bodies being charged with equal and similar quantities of electricity. In every other case, although the charges may be of the same sign, the question of whether we have attraction or repulsion depends on the ratio of the charges on the bodies, say spheres, the

ratio of their diameters, and the distance from centre to centre. A closer study of the values of the forces in various cases opens up a whole vista of possibilities for the play of either attractions or repulsions between the drops such as we are considering here (see Kelvin * and Rayleigh †).

It is hardly possible to treat mathematically the case for more than two bodies; even the problem of two equal spheres at a given distance from each other offers an exceedingly laborious solution. The formulæ for the force between two spheres of radii a and b , at potentials u and v respectively, the distance from centre to centre c , have been deduced in probably the simplest form by Lord Kelvin ‡ by use of the method of electrical images. For a system of two conductors of potential u and v , bearing charges D and E respectively,

$$D = q_{11}u + q_{21}v, \quad E = q_{12}u + q_{22}v, \quad \dots \quad (1)$$

where q_{11} and q_{22} are the coefficients of capacity and $q_{21} = q_{12}$ is the coefficient of induction. For the spheres (radii a and b , at distance centre to centre c)

$$\left. \begin{aligned} q_{11} &= \frac{1}{P_1} + \frac{1}{P_2} + \frac{1}{P_3} + \dots, \\ q_{22} &= \frac{1}{Q_1} + \frac{1}{Q_2} + \frac{1}{Q_3} + \dots, \\ q_{21} &= q_{12} = -\frac{1}{S_1} - \frac{1}{S_2} - \frac{1}{S_3}, \end{aligned} \right\} \dots \quad (2)$$

where the successive values of each of the P 's, Q 's, and S 's are given by the general formula:

$$X_{n+1} = \frac{c^2 - a^2 - b^2}{ab} X_n - X_{n-1}. \quad \dots \quad (3)$$

The values of the first terms for P , Q , and S are deduced by Kelvin to be

$$\left. \begin{aligned} P_1 &= \frac{1}{a}, & Q_1 &= \frac{1}{b}, & S_1 &= \frac{c}{ab}, \\ P_2 &= \frac{c^2 - b^2}{a^2b}, & Q_2 &= \frac{c^2 - a^2}{ab^2}, & S_2 &= \frac{c^2 - a^2 - b^2}{ab} S_1. \end{aligned} \right\} \dots \quad (4)$$

The value of the force between the two spheres is given by

$$F = \frac{1}{2} \left\{ u^2 \frac{dq_{11}}{dc} + 2uv \frac{dq_{21}}{dc} + v^2 \frac{dq_{22}}{dc} \right\}, \quad \dots \quad (5)$$

* Papers on Electrostatics and Magnetism, 1884.

† Sc. Papers, ii. p. 103.

‡ Electrostatics and Magnetism, pp. 96-97, ¶ 142.

being repulsion or attraction according as the sign of the total is positive or negative. As these formulæ are perfectly general they can be used to give the force between two spheres for any values of a , b , and c .

Kelvin* has published the values of the constants involved in the case of two equal spheres at distances from centre to centre from twice the radius of the spheres, *i. e.*, the spheres touching, to distance four times the radius. In this case the calculation is simplified because $q_{11} = q_{22}$. Putting

$$\Sigma \frac{1}{P} = Ir \quad \text{and} \quad \Sigma \frac{1}{S} = Jr,$$

where r is the radius of the spheres, Kelvin gives the following equations to calculate the charges D and E from the potentials u and v , and the force in terms of either u and v or D and E

$$D = (Iu - Jv)r, \quad E = (-Ju + Iv)r, \quad . \quad . \quad . \quad (6)$$

$$F = 2Buv - A(u^2 + v^2), \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$F = \frac{1}{r^2} \{ 2\beta DE - \alpha(D^2 + E^2) \}, \quad . \quad . \quad . \quad . \quad (8)$$

where I , J , B , and A may be calculated from as many terms of the above series as necessary, and where α and β are given by

$$\alpha = \frac{A(I^2 + J^2) - 2BIJ}{(I^2 - J^2)^2} \quad \text{and} \quad \beta = \frac{B(I^2 + J^2) - 2AIJ}{(I^2 - J^2)^2} \quad . \quad . \quad (9)$$

As a typical case, we have calculated, using the formulæ above, the corresponding constants for the case $a = 2r$, $b = r$, $c = 3.5r$; *i. e.*, one sphere twice the other, and the distance apart of nearest points half the radius of the smaller sphere. Of course, in this case q_{22} is no longer equal to q_{11} and the corresponding equations showing the relation between the potentials and the charges, and the value of the force in terms of the potentials and the charges, become

$$D = (Iu - Jv)r, \quad E = (-Ju + Kv)r \quad . \quad . \quad . \quad (10)$$

where $Kr = \Sigma 1/Q$, r being the radius of the smaller sphere ;

$$\left. \begin{array}{l} \text{and} \quad F = -Au^2 + 2Buv - Cv^2, \\ \text{or} \quad F = \frac{1}{r^2} \{ -\alpha D^2 + 2\beta DE - \gamma E^2 \} \end{array} \right\} \quad . \quad . \quad . \quad (11)$$

* Electrostatics and Magnetism, pp. 96-97, ¶ 142.

where I, J, K, A, B, and C may be calculated as before and

$$\left. \begin{aligned} \alpha &= \frac{AK^2 - 2BKJ + CJ^2}{(IK - J^2)^2}, \\ \gamma &= \frac{AJ^2 - 2BJI + CI^2}{(IK - J^2)^2}, \\ \beta &= \frac{B(J^2 + IK) - AJK - CJI}{(IK - J^2)^2}. \end{aligned} \right\} \dots \dots (12)$$

For this case ($a=2r$, $b=r$, $c=3.5r$), to a close approximation,

$$\left. \begin{aligned} I &= 2.5, & J &= .79, & K &= 1.34, \\ A &= .26, & B &= .27, & C &= .21, \\ \alpha &= .0035, & \beta &= .052, & \gamma &= .055. \end{aligned} \right\} \dots \dots (13)$$

The interest of these equations, (1) to (13), is twofold. (1). Using the expressions for the forces we may calculate whether in any given circumstances of size, charges, and distance apart we shall have attraction or repulsion between the two spheres. (2). In the manner in which the streams are always charged we can obtain the effect of the charge on the drop just leaving the unbroken stream on the value of the charge given to the next drop to be formed.

1. Although, as the accompanying photographs show, we cannot be dealing exclusively with the simple case of two equal spheres, the manner in which the attraction or repulsion varies with the ratio of the charges on the equal spheres for constant distance apart, or with the distance apart for a constant ratio between the charges, will give some insight into the similar effects for unequal spheres. The numbers given in Table I. for c , α , and β are taken from Lord Kelvin's results, and the value of the force between unit spheres is calculated for various distances between the spheres and simple ratios $D : E$ from 1 : 1 to 6 : 1. The curve in fig. 12 shows the relation between the force between two equal spheres ($D : E = 6 : 1$) and the distance from centre to centre; i. e., the numbers of column 9 plotted against those of column 1.

It is very apparent that as the spheres approach the forces of attraction increase with great rapidity, while on the other hand, as the distance is increased beyond the point of neutrality, the value of the repulsive force grows very slowly. That is the attractive forces at small distances will be made

TABLE I.

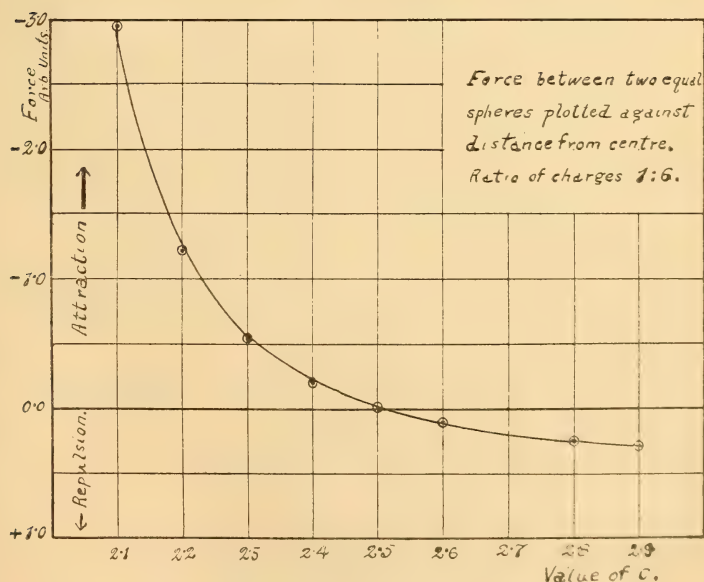
Values of α and β in Equation for two equal spheres

$$F = \frac{1}{r^2} \{2\beta DE - \alpha(D^2 + E^2)\}.$$

Given value of ratio D : E, $F = \frac{1}{r^2} \cdot E^2 \cdot f(\alpha\beta)$.Values of $f(\alpha\beta)$ for various ratios D : E.

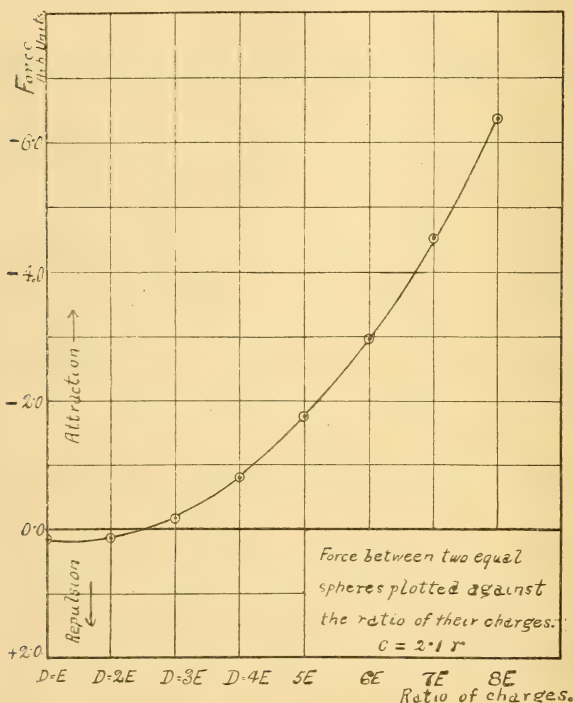
c .	α .	β .	D=E 2 β - 2 α .	D=2E 4 β - 5 α .	D=3E 6 β - 10 α .	D=4E 8 β - 17 α .	D=5E 10 β - 26 α .	D=6E 12 β - 37 α .
2.1	.15375	.22668	+ .14586	+ .13797	- .18742	- .80031	- 1.7307	- 2.96859
2.2	.08263	.15251	positive	positive	+ .08876	- .18463	- .62328	- 1.22719
2.3	.05444	.12186	"	"	positive	+ .04936	- .19684	- .55196
2.4	.03955	.10309	"	"	"	positive	+ .00026	- .22617
2.5	.02997	.09038	"	"	"	"	+ .12458	- .02433
2.6	.02342	.08078	"	"	"	"	positive	+ .10282

Fig. 12.



much more apparent than the repulsive forces. Again, fig. 13 gives the numbers of the first row of the table plotted against the ratio of the charges. Here again we see that as the values of the charges differ more and more, the attractive forces will be much more apparent than the repulsive forces were.

Fig. 13.



That these forces are extremely important in the cases under consideration is borne out by numerical calculation for two typical cases:—

1. Suppose two equal drops .1 cm. in radius at distance centre to centre of .23 cm. ($r = .1$, $c = 2.3$). From Kelvin's tables in expression for force (8)

$$\alpha = .05444, \quad \beta = .12186,$$

and

$$F = \left\{ 12\beta - 37\alpha \right\} \frac{E^2}{r^2}, \text{ if } D : E = 6 : 1.$$

If E is charge sufficient to raise the isolated spherical drop to say, $+100$ volts,

$$E = Vr = \frac{1}{30} \text{ E.S. unit.}$$

$$\therefore F = -.552 \times \frac{1}{30^2} \times 10^2 = -.061 \text{ dyne (attraction).}$$

The weight of one drop $= \frac{4}{3} \pi r^3 \rho g = \text{approx. } 4 \text{ dynes.}$

Electrical force is then $\frac{6}{400}$ of the weight of drop.

2. Suppose two unequal drops, $a = .2 \text{ cm.}$, $b = .1 \text{ cm.}$, and $c = .35 \text{ cm.}$ If the quantity on smaller drop would raise it to 100 volts if it were isolated, and if $D = E$,

$$E = \frac{1}{30} \text{ E.S. unit.}$$

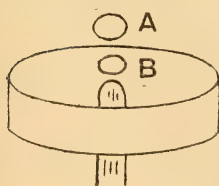
From equation (11),

$$F = \frac{2\beta DE - \alpha D^2 - \gamma E^2}{r^2} = + \frac{.0455 \times 10^2}{30^2} = +.005 \text{ dyne (repulsion).}$$

(2) The question now arises "Is there any ground for believing that in the cases before us we have really two drops bearing charges for which the ratio becomes very large?" Here it would be well to examine the conditions at the point of breaking of the stream.

From such photographs as shown in figs. 2, 8 c, 9 c, we see, as to size and distance apart, the relation between drops as they break from the stream. From what has been said above we must conclude that there will be strong forces between the drop which has just left and the one that is just forming, and that the charge on the drop leaving will have an influence on the size of the charge on the drop just forming.

Suppose A and B to be two consecutive drops which, for simplicity, we shall first suppose equal to one another and of



radius $r \text{ cm.}$ They are forming at the centre of a ring maintained at a potential $+V$ volts. The potential at centre of ring will be, approximately, $2/\pi V$, say $2/3V$. If A has just left the stream at potential zero, and no drops are close above it, it will have a negative charge approximately sufficient to give it a potential $-2/3V$ if it were

far removed from all other conductors. The charge on A is

Phil. Mag. S. 6. Vol. 23. No. 133. Jan. 1912. M

then given by

$$D = -2/3 V r.$$

But from equation (6), if B is distant, centre to centre, cr from A, the charge E on B due to charge D on A will be given by

$$\begin{aligned} D &= (Iu - Jv)r, \\ E &= (-Ju + Iv)r. \end{aligned}$$

But just as it breaks away B is at zero potential: putting then $v=0$ we have

$$D = Iur, \quad E = -Jur.$$

From which

$$E = -\frac{J}{I} \cdot D = +\frac{J}{I} \cdot \frac{2}{3} \cdot V r.$$

For the distance from centre to centre equal to $2.5 r$, just as B breaks away,

$$\frac{J}{I} = \frac{.52537}{1.25324} = .42.$$

$$\therefore E = +.42 \left(\frac{2}{3} V r \right).$$

But if the drop B came off singly, it would have approximately a potential $-2/3V$ and consequently a charge $-2/3Vr$, induced by the inductor tube. The total charge, E' , on B will then be

$$E' = -\frac{2}{3} V r + .42 \left(\frac{2}{3} V r \right) = -.58 \left(\frac{2}{3} V r \right).$$

Ratio of charges D and E' on drops A and B is $1.7 : 1$.

As our photographs show there is a variation in the sizes of the drops leaving the stream. The effect of a large drop on a succeeding small one is much more noticeable than the above case of equal drops. Let radii of A and B be respectively $2r$ and r and the potential of A as it leaves be the same as before. Then if the nearest point of the drop A is $.5r$ distant from boundary of B, just as the latter breaks away, we have the case of two drops (equation 10), in which

$$a=2r, \quad b=r, \quad \text{and} \quad c=3.5r.$$

If potential of A is $-2/3V$, the value of charge D on A is

$$-2/3V \cdot 2r = -2 \left(\frac{2}{3} V r \right).$$

From equations (10), putting potential of B equal zero ($v=0$), we have

$$\begin{aligned} D &= Iur, \\ E &= -Jur, \quad E = -\frac{J}{I} \cdot D. \end{aligned}$$

For the particular case

$$\frac{J}{I} = \frac{.79}{2.5} = .31,$$

$$\therefore E = -.31D = +.62\left(\frac{2}{3}Vr\right).$$

Again, if drop B came off singly, it would have a potential approximately equal to $-2/3 V$ and consequently a charge equal to $-2/3 Vr$ induced by the inductor tube. That is, the net charge, E' , on the drop B is

$$-\left(\frac{2}{3}Vr\right) + .62\left(\frac{2}{3}Vr\right) = -.38\left(\frac{2}{3}Vr\right).$$

The ratio of the charges D and E' on A and B will be

$$D : E' = 2 : .38 = 5.3 : 1.$$

Reversing the order in which A and B leave the stream so as to have the smaller one escape first, the effect of B on the potential of A will be proportionally much smaller. From equations (10), putting $u=0$ we have

$$D = -Jvr, \quad E = +Kvr,$$

$$D = -\frac{J}{K} \cdot E = +\frac{J}{K} \cdot \left(\frac{2}{3}Vr\right).$$

For this particular case

$$a=2r, \quad b=r, \quad c=3.5r, \quad \frac{J}{K} = \frac{.79}{1.34} = .59.$$

The charge given to A by the inductor ring is $-2/3 \cdot V \cdot 2r$, therefore net charge, D' , on A is

$$-2\left(\frac{2}{3}Vr\right) + .59\left(\frac{2}{3}Vr\right) = -1.41\left(\frac{2}{3}Vr\right),$$

which leaves the ratio of $D' : E = 1.41 : 1$.

It is apparent from these facts that in consideration of accidental causes which influence the breaking of the streams (Rayleigh*) we may expect to have in the stream drops large and small bearing charges of same sign (or it is conceivable of opposite sign) having almost any ratio; as a consequence in general for small distances we shall have attractions of greater or less force and at great distances repulsions.

* Sc. Papers, ii. p. 103.

We may now recall for electrified streams the experimental facts which require explanation :—

1. The alignment of all electrified streams for a certain distance beyond the inductor ;
2. The coalescence of the drops for smaller voltages on the inductor ; and
3. The mutual repulsion of the drops at higher voltages.

(1) *Alignment.*

Two elements enter in to cause this alignment. In a succession of drops, such as in figs. 2 and 9 *b*, it is likely that the forces of attraction between the neighbouring drops are sufficient to carry them along identically the same path. Again, as is shown by the influence of vibrating bodies on the breaking stream, if the drops are sent off under initially the same conditions they will travel over the same course. Now just as the drops form they will be under the strong attraction of those just leaving, and, also, just as they break from the main continuous column they will be strongly attracted to it by the force deducible from equation (11) ; if any drop then has initially a tendency to diverge from the general path it will be pulled back. Consequently all the drops will be given their velocities in the same initial direction.

(2) *Coalescence.*

Keeping in mind these electrostatic forces, no difficulty should be found in the explanation of coalescence. When two drops bearing unequal charges, or two unequal drops bearing equal charges, are brought closely enough together there are immensely strong, increasing forces of attraction between them and coalescence will surely take place if the resulting drop is not too large to be unstable. One would expect that at the moment of collision there would be an electric discharge between the two adjacent spheres. Many influences conspire to bring the drops in the stream closer and closer together. If in a stream the velocity of the drops is sufficient to carry them a vertical distance of 10 cm., two drops breaking away $1/1000$ of a second apart will be distant from one another approximately $\cdot 14$ cm. at the beginning of their journey. When the first one has reached the top of its course, taking into consideration only gravity, the distance between the drops will be approximately 5×10^{-4} cm. Again the friction of the air for a given velocity will cause a greater retardation in the case of small drops than in the case of large ones, which will tend to bring a large drop nearer to the smaller one ahead of it.

(3) *Repulsion.*

It has been noted in figs. 6, 7, 9 *c*, 10 *a*, and 10 *b* that scattering takes place in the stream, in one case (9 *c*) rather suddenly. This must be due to the repulsion between the drops. Two choices offer themselves. The drops may be during their whole journey at distances for which the force acting between them is repulsive; but on account of the velocity with which they leave the nozzle they travel a certain distance in the aligned stream before the repulsive forces due to their neighbours are strong enough to cause divergence from the path which they would traverse under gravity. This view seems to be favoured by the phenomena observable in figs. 6 and 7; the scattering becomes apparent much more quickly at high voltages than at low.

As was pointed out above, it is possible that in the case of higher voltages we have the coalescence of the drops due to attractions, the formation of large drops which are unstable under such large electrical forces and consequently break into smaller drops. This view seems to be favoured by the abundance of small, almost uniformly sized drops (fig. 10 *b*) at the point of greatest scattering of the stream charged by the inductor at 720 volts (fig. 6).

We desire to express our thanks to Professor J. C. McLennan whose lectures on Properties of Matter first suggested the problem, and who has cooperated, as always, by placing the resources of the laboratory for our use as necessity arose.

University of Toronto,
Department of Physics,
August, 1911.

XIII. *On Opalescence of Gases in the Critical State.* By M. S. SMOLUCHOWSKI, Ph.D., LL.D. (Glasgow), Professor of Theoretical Physics, University of Lemberg*.

THE number for November 1910 of this Magazine contains an account of F. B. Young's careful experimental investigation "On the Critical Phenomena of Ether," including some valuable observations on the critical opalescent phenomena, and a discussion of the various theoretical explanations hitherto suggested. Its author appears, however, to have overlooked a kinetic theory of opalescence which I expounded in a paper published in 1907†, and which has

* Communicated by the Author.

† *Bulletin Intern. Acad. Cracovie*, Dec. 1907; *Ann. d. Phys.* xxv. p. 205 (1908).

been discussed since by some authors. As this theory leads to definite quantitative conclusions, calling for experimental verification, I may be allowed to give a brief summary of it and some further developments* relating to its control by observation.

The kinetic theory of opalescence is based on the self-evident, as I think, supposition that the molecules in gases and liquids (also in solids) cannot be distributed quite uniformly in space, but are subjected to a process of ever changing local agglomeration and dispersion, as a consequence of their molecular movements. Let us denote the deviation from normal uniform density by δ , so that the ratio of the number n of molecules actually contained in a given volume to the number ν contained in case of uniform distribution is given by $n/\nu = 1 + \delta$, then it can be shown easily† that in ideal gases the probability of a deviation between the limits δ and $1 + \delta$ is

$$W(\delta) d\delta = \sqrt{\frac{\nu}{2\pi}} e^{-\frac{\nu\delta^2}{2}} d\delta,$$

and that the mean square of the deviation in density is

$$\overline{\delta^2} = 1/\nu,$$

being thus exceedingly minute under normal conditions, except for submicroscopic volumes. This is a special case of the general formula, applicable to a substance following any given characteristic equation

$$W(v) = b e^{\frac{v}{R\theta_0}} \int_{v_0}^v (p - p_0) dv_0 \dots \dots (1)$$

(R being the gas constant for one gram substance), which defines the probability of ν molecules having a specific volume v , when its normal value is v_0 . The exponent, which is identical with the work done by isothermal compression of 1 gr. substance from its normal specific volume, for uniform density, to the considered value, can be developed in a series after ascending powers of $(v - v_0) = -v_0\delta$,

$$\int_{v_0}^v (p - p_0) dv = \frac{v_0^2 \delta^2}{2} \left(\frac{\partial p}{\partial v} \right)_0 - \frac{v_0^3 \delta^3}{3!} \left(\frac{\partial^2 p}{\partial v^2} \right)_0 + \dots \dots, \quad (2)$$

* Extracted from *Bulletin Intern. Acad. Cracovie*, Juillet 1911.

† M. Smoluchowski, *Boltzmann-Festschrift*, p. 626 (1904); the formula requires some modification if ν is not a large number. Cf. Bateman, *Phil. Mag.* xxi. p. 748 (1911), and also Svedberg and Inouye, *Zeitsch. Phys. Chem.* lxxvii. p. 145 (1911).

while the constant b is got by performing the integration over all possible values of δ . Thus we get the approximate mean square of the deviation in density

$$\overline{\delta^2} = \frac{R\theta_0}{\nu_0^2 \left(-\frac{\partial p}{\partial v} \right)_0} \cdot \cdot \cdot \cdot \cdot \quad (3)$$

We see that the tendency to local agglomerations is excessively great in the immediate neighbourhood of the critical point, where the terms with $(\partial p / \partial v)_0$ and $(\partial^2 p / \partial v^2)_0$ are vanishing, so that this formula has to be corrected by taking into account the fourth power of δ .

These agglomerations and rarefactions must give rise to corresponding local deviations of the index of refraction from its mean value, and thus the coarse-grainedness of the substance must reveal itself by Tyndall's phenomenon, with a very pronounced maximal value at the critical point. In this way the critical opalescence explains itself very simply as the result of a phenomenon the existence of which cannot be denied by anybody accepting the principles of the kinetic theory, even if exception be taken to the above quantitative formulæ, derived from theoretical considerations which cannot be set forth here in detail.

Rothmund*, who has given valuable experimental contributions to this subject, prefers Donnan's capillary theory of these phenomena, but he does not put forward any argument against the above explanation, except perhaps a general dislike of kinetic theory which nowadays will hardly be considered as very conclusive. There is the common supposition of coarse-grainedness underlying both theories, and it is proved, indeed, by Tyndall's phenomenon. Donnan, however, and in general those authors who cling also for this case to the thermodynamic conception of definite separate phases, must consider the opalescent substance as an emulsion of one phase in another, both being physically different, homogeneous substances, and are forced to admit *ad hoc* invented highly artificial and questionable suppositions about capillary tension at the surface of separation.

According to the kinetic theory, on the contrary, the thermodynamic macroscopic conceptions of phases, surfaces of separation, and surface-tension are altogether inapplicable to this case; there are no discontinuities of phase, only continuous transitions, ever changing diffuse agglomerations, governed by the laws of statistical equilibrium. According to it the phenomenon of critical opalescence is intrinsically

* *Zeitsch. Phys. Chem.* xxvi. p. 433 (1898); lxiii. p. 54 (1908).

the same as Rayleigh's blue of the sky, and will transform into it in a continuous manner with elevation of temperature.

The first attempt at a kinetic explanation is that given by Küster, with which I became acquainted through F. B. Young's paper. But I think its inadequacy is apparent by comparison with the above theory. For the immediate cause of opalescence are differences of (optical) density, not of temperature; differences of temperature could act only in an indirect way, by influencing density. But deviations in density must exist, quite independently of Maxwell's deviations in temperature, since they are a necessary direct outcome of the chance grouping of molecules.

The kinetic theory given above is the only one yielding any definitive quantitative relations, while nothing of this kind is to be expected from the capillary theory, as it rests on a wholly arbitrary and uncontrollable supposition. They have been controlled, with a favourable result in general, in a very important experimental research by Prof. Kamerlingh-Onnes and Dr. Keesom*.

I had pointed in my paper on Lord Rayleigh's formula for the index of absorption h of a medium containing in unit volume n particles of volume T

$$h = \frac{32}{3} \pi^3 \frac{n T^2}{\lambda^4} \left(\frac{\Delta \mu}{\mu} \right)^2 \dots \dots (4)$$

as defining the absorption by the coarse-grained substance, when connected with the above formulas for the deviations in density, and with the known relation between the index of refraction μ and the density, and I had drawn some quantitative conclusions therefrom, without however writing down the explicit final formula, for I considered it only as indicating roughly the order of magnitude, since our case presents some peculiarities not fitting at all with the suppositions underlying Rayleigh's calculation.

Einstein, however, has arrived in a very remarkable way by explicit calculation of the components of the dispersed waves at the same formula which follows from the above reasoning†, namely

$$h = \frac{8\pi^3}{27} \frac{[(\mu^2 - 1)(\mu^2 + 2)]^2}{\lambda^4} \frac{H\theta}{N} \left(-\frac{\partial v}{\partial p} \right) \dots (5)$$

* Comm. from Phys. Lab. Leiden, No. 104, p. 15 (1908).

† Einstein, *Ann. d. Phys.* xxxiii. p. 1275 (1910), his formula (18), p. 1293. The numerical result for air given by me, *Ann. d. Phys.* xxv. p. 216 (1908), is vitiated by a slip of calculation, the value ought to be doubled. [Addendum] Keesom has published now a short reprint of the above paper (*Ann. d. Phys.* xxxv. p. 591, 1911), where the deduction of this formula is given in full.

[H denoting the gas constant for 1 gr. molecule, N the number of molecules in 1 gr. molecule].

Now the intensity of the opalescent light s , which is scattered into unit conical angle in a perpendicular direction to the incident light (its intensity being put equal to unity), is connected with this magnitude by the relation

$$s = \frac{3}{16\pi} h, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and this is the quantity which Kamerlingh-Onnes and Keesom have measured experimentally for ethylene, at temperatures ranging from $0^{\circ}06$ to $2^{\circ}41$ above its critical point. A detailed comparison of their results and those got for ether by F. B. Young is not possible, as the latter ones are published only in a rough graphical way, but the general outline of the curve defining the opalescence as function of the temperature is quite analogous (except the extrapolated part for the immediate neighbourhood of θ_c).

The authors compare it with the above theory by introducing the value of $v \frac{\partial p}{\partial v}$ given by Verschaffelt* for the neighbourhood of the critical point

$$v \frac{\partial p}{\partial v} = -10 \frac{p_0}{v_0} (\theta - \theta_c),$$

and find an approximate agreement, both considering the relative values of s as depending on $(\theta - \theta_c)$, and also its absolute value.

As a repetition and extension of such measurements is highly desirable (with special precautions respecting purity of the substance, which has been demonstrated by F. B. Young to be a very important factor), it may be worth while to consider more in detail the results we should expect for a substance following, for instance, Van der Waals' reduced equation

$$\pi = \frac{8\phi}{3\phi - 1} - \frac{3}{\phi^2}.$$

In the neighbourhood of the critical point $\pi = \phi = \phi_c = 1$ it assumes the approximate form

$$\Delta\pi = 4\Delta\phi \left[1 - \frac{3}{2} \Delta\phi + \frac{9}{4} \Delta\phi^2 \right] - \frac{3}{2} \Delta\phi^3,$$

where $\Delta\pi = \pi - 1 = \frac{p - p_c}{p_c}$ &c., and the development (2) then

* Verschaffelt, Comm. from Phys. Lab. Leiden, Supplm. No. 6, p. 3 (1903).

is approximately given by

$$\int_{v_0}^{v_0(1-\delta)} (p-p_0) dv = -p_c v_c \left[\frac{\delta^2}{2} (6\Delta\vartheta - 18\Delta\vartheta\Delta\phi + \frac{9}{2}\Delta\phi^2) + \frac{\delta^3}{3!} (18\Delta\vartheta - 9\Delta\phi) + \frac{9\delta^4}{4!} \right].$$

The third power of δ is generally negligible, and so will be the fourth power too, provided $\Delta\vartheta$ is large compared with $\delta^2/8$. It is not easy to define exactly the limits of this restriction, as δ^2 depends on the size of the volume considered. If we calculate δ^2 by means of (3) for a volume of a wave-length cube, which may perhaps give a rough idea of it, we should come to the conclusion that the neglect of δ^4 is legitimate, except within the distance of $\frac{1}{100}$ degree from the critical temperature, but I should not venture any definite statement thereon until the complete theory for this case is worked out. The effect of the term with δ^4 would be to give smaller values for the opalescence than for the simplified formula, especially for the shorter wave-lengths, which may influence also the colour of opalescence; but it is possible too that the deviations from the proportionality to the inverse fourth power of λ (Rayleigh's blue) observed by Kamerlingh-Onnes and Keesom within $0^{\circ}5$ of θ_c may be due rather to the fact that at such temperatures the elements of space in which the deviation from uniform density is considerable are no longer small in comparison with λ —as supposed in the above theory.

Without going into these questions now, let us suppose in the following that we observe the opalescence at such a distance from the critical point that the neglect of the term with δ^4 is legitimate. In this case formula (5) remains valid, with substitution of

$$\frac{\partial p}{\partial v} = -6 \frac{p_c}{v_c} \left[\Delta\vartheta (1 - 3\Delta\phi) + \frac{3}{4} \Delta\phi^2 \right], \quad . \quad . \quad (7)$$

and the dependence on temperature and specific volume can be represented by a system of hyperbolic, "iso-opalescent" curves

$$s[\Delta\vartheta - 3\Delta\vartheta\Delta\phi + 3/4\Delta\phi^2] = \text{const.} \quad . \quad . \quad (8)$$

Now let us imagine the substance to be contained in a Natterer tube and its temperature slowly decreasing until separation into two phases takes place. The temperature where this occurs for a given $\Delta\phi$ is determined by the equation of the border curve, which can be deduced in

various ways* by aid of Maxwell's well-known condition. Developing all variables in series in the neighbourhood of the critical point we get the reduced specific volumes in the liquid and gaseous state as functions of the absolute value $\Delta\tau$ of the distance from the critical temperature

$$\phi_1 = 1 - 2\sqrt{\Delta\tau} + \frac{18}{5}\Delta\tau,$$

$$\phi_2 = 1 + 2\sqrt{\Delta\tau} + \frac{18}{5}\Delta\tau.$$

Thus the apparent critical temperature, when the meniscus appears at the lower or higher end of the Natterer tube according as $\Delta\phi \gtrless 0$, is less than the true critical temperature by $\Delta\tau = \frac{\Delta\phi^2}{4}$, and the opalescence in this state will be inversely proportional to the value

$$\frac{\partial p}{\partial v} = -6 \frac{p_c}{v_c} \left[\frac{\Delta\phi^2}{2} + \frac{3}{4}\Delta\phi^3 \right] = -12 \frac{p_c}{v_c} \left[\Delta\tau \pm \frac{3}{4}\Delta\tau^{3/2} \right], \quad (9)$$

being thus slightly greater for negative than for positive values of $\Delta\phi$.

For higher temperatures (the one-phase state) we can replace (7) approximately by

$$\frac{\partial p}{\partial v} = -6 \frac{p_c}{v_c} [\Delta\vartheta + 2\Delta\tau], \quad . \quad . \quad . \quad . \quad (10)$$

if $\Delta\vartheta$ denotes the excess of the actual temperature over the apparent critical temperature. But if the temperature falls below the point of separation by $\Delta\vartheta$ we must put

$$\frac{\partial p}{\partial v} = -6 \frac{p_c}{v_c} [2\Delta\vartheta + 2\Delta\tau]. \quad . \quad . \quad . \quad . \quad (11)$$

Thus we see : 1. For a given temperature the opalescence is smaller, if the specific volume is greater or less than the critical volume (in accordance with former observations).

2. The opalescence of the two coexisting, liquid and gaseous, phases is roughly equal; by taking into account higher terms it is found to be smaller for the gaseous state.

3. The opalescence diminishes more slowly (twice as slow if $\Delta\phi = 0$), when the temperature rises above the point of separation than when it falls below it.

The same conclusions remain substantially valid if we

* See *f. i. Kuenen, Zustandsgleichung* (Vieweg, Braunschweig), p. 92.

introduce the empirical coefficients given by Verschaffelt (*loc. cit.*) instead of Van der Waals' equation, only the numerical values have to be changed. The equation of the border curve is then given by

$$\phi = 1 \mp 3.37 \sqrt{\Delta\tau} + 10.9 \Delta\tau.$$

For points in the one-phase space we get, instead of (10),

$$\frac{\partial p}{\partial v} = -\frac{p_c}{v_c} [10 \Delta\mathfrak{S} + 18.4 \Delta\tau]; \quad . \quad . \quad . \quad (12)$$

for the two-phase state, instead of (11),

$$\frac{\partial p}{\partial v} = -18.4 \frac{p_c}{v_c} [\Delta\mathfrak{S} + \Delta\tau]; \quad . \quad . \quad . \quad (13)$$

for the point of separation into two phases

$$\frac{\partial p}{\partial v} = -\frac{p_c}{v_c} [18.4 \Delta\tau \mp 28.9 \Delta\tau^{3/2}], \quad . \quad . \quad (14)$$

where the upper and lower sign relate to a specific volume smaller or larger respectively than the critical volume.

The quantitative measurements of opalescence, alluded to above, have been made hitherto only for the one-phase state, and they were compared with theory under the assumption that the specific volume had exactly the critical value ($\Delta\phi = \Delta\tau = 0$). As this seems a somewhat doubtful point, which according to the above formulas may be of considerable importance, measurements on several tubes, with different values for the specific volume, are very desirable.

To make analogous observations in the two-phase state will be much more difficult, as the establishment of thermic equilibrium is a much slower process there, owing to the thermal effects of local evaporation or condensation. F. B. Young's paper demonstrates in a very instructive way the persistency of minute thermal inequalities and the enormous importance of this factor. No doubt also the fact observed by Travers and Usher and F. B. Young, that for slowly rising temperature the opalescence of the "receding" phase is greater, is to be explained in this way. Mr. Young rightly observes (p. 813) that the density of the receding phase must approach the critical density when the meniscus is disappearing, which can be explained by those thermal effects; this means that its temperature must be higher than that of the increasing phase, and therefore more favourable for opalescence.

Approximate equality of opalescence in both phases ought

to be a very sensitive indicator of thermal equilibrium. It is questionable, indeed, whether it ever has been observed hitherto. Finally, as regards conclusion (3), it seems to be corroborated by Young's remark (p. 814) about a wider limit of opalescence for positive than for negative deviations from the critical temperature.

It may be noted that a similar theory refers to the analogous phenomena near the critical point of separation of binary mixtures*. The opalescence of the two coexisting liquid phases below this point does not seem to have been observed hitherto, no doubt only owing to the difficulty of establishing the equilibrium of concentration.

Experimental work on these phenomena is of considerable theoretical importance, since, according to the kinetic theory, they are a direct evidence of a quality of matter out of reach of ordinary thermodynamics: its intrinsic inhomogeneousness. Besides, the determination of the opalescent curves ought to be the most exact method of determining critical temperature and density, and generally of the shape of the equation of state in the neighbourhood of the critical point.

XIV. *The Charges on Thermions produced in Air and Hydrogen at Atmospheric Pressure.* By J. C. POMEROY, M.A., Fellow in Physics, Princeton University †.

IN view of the work done by O. W. Richardson and F. C. Brown ‡ on the value of the specific charge and the kinetic energy of positive and negative thermions it was thought advisable to determine the value of the charge itself. It was intended to make some preliminary tests in air at atmospheric pressure, and in some other gases, and then try the effect of reducing the pressure. However, some results were obtained at atmospheric pressure which, while of no special meaning in connexion with the experiments made at low pressures already referred to, have still some little interest in themselves. The method adopted was practically that used by Townsend § in his work on the ions produced by secondary Röntgen radiation. The essential part of the

* Cf. Smoluchowski, *Ann. d. Phys.* xxv. p. 219 (1908); Einstein, *Ann. d. Phys.* xxxiii. p. 1295 (1911).

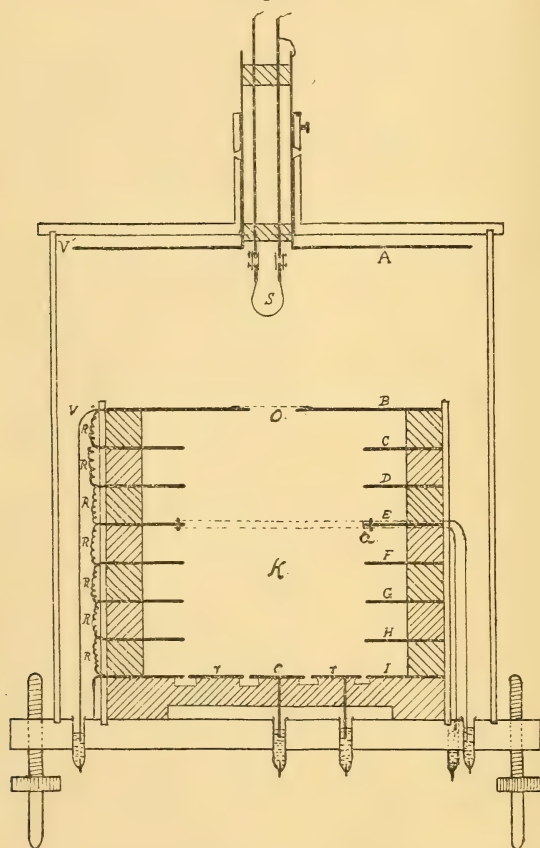
† Communicated by Prof. O. W. Richardson.

‡ O. W. Richardson and F. C. Brown, *Phil. Mag.* Sept. 1908; *Phil. Mag.* Nov. 1908, Dec. 1908, Nov. 1909. F. C. Brown, *Phil. Mag.* Oct. 1909.

§ J. S. Townsend, *Roy. Soc. Proc. A.* vol. 81, p. 464.

method is to have the ions moving in a uniform field and then examine the distribution in some particular case. A vertical section of the apparatus used is shown in figure 1.

Fig. 1.



The ions given off by the heated strip *S* pass downward under the action of the field and part of them pass through the opening in plate *B*, which was covered by a grating of fine wire. The stream of ions then opens out so that part fall on the central disk *c* and the remainder on the ring *r*, and the ratio of these two quantities Q_c/Q_r was measured by connecting first one and then both disk and ring to an electrometer, when the ratio Q_r/Q_c is given by

$$Q_c/Q_r \text{ or } Q_r/Q_c = C_2 V_2 / C_1 V_1 - 1,$$

according as the ring *r* or the disk *c* is first connected to

the electrometer. In the above C_1 , V_1 , C_2 , and V_2 are the capacities and potentials of the system first connected to the electrometer and of the whole system respectively.

A uniform field in the chamber K was maintained in the following way:—A series of flat brass rings B, C, ... I were placed 1 cm. apart and connected by equal high resistances. B was raised to a potential V and I was earthed.

A was raised to a potential V' higher than V and of the same sign. The ring r and the disk c were cut from the same sheet of brass so as to avoid any chance of contact potential between them and their potential in no case differed much from zero.

A theory for the distribution of the ions has been worked out by Townsend* from Maxwell's equations for the diffusion of one gas into another. An outline of this is given below. In this theory it is assumed that the partial pressure of the ions is not appreciably greater than that of an equal number of molecules, but in Townsend's experiments the distribution was found to fit in with the theory except for negative ions where the pressure was low and the gas very dry, and in the present experiments it was found that no correction need be made in any case.

When a uniform stream is passing through the aperture O, the partial pressure (p) of the ions at any point in the field of uniform force Z is given by the equation,

$$\nabla^2 p = \frac{NeZ}{\Pi} \frac{dp}{dz},$$

where N is the number of molecules per cubic centimetre in a gas at atmospheric pressure Π and a temperature equal to that of the gas in the experiments.

The solution of this equation is given by $p=f(N.e.Z)$, but where the assumption made above is correct and n = the number of ions per c.c. $p=\Pi n/N$. Whence $n=\phi(N.e.Z)$, in which all the constants are functions of the coordinates of the position of the point, *i.e.* of r and z .

In the experiments $z=h$, and therefore

$$\frac{Q_c}{Q_r} = \frac{\int_0^a rn \, dr}{\int_a^b rn \, dr},$$

where a and b are the radii of the disk and ring respectively.

* J. S. Townsend, Roy. Soc. Proc. A. vol. 80, p. 207.

Hence the method gives a method of determining the value of $\phi(N.e.Z)$.

It was not necessary for the purpose of this investigation to determine the form of this function, for in these experiments the method was to compare :

- I. The value of Q_c/Q_r given by ions from various sources, and
- II. The value of Z necessary to give Q_c/Q_r a constant value for these different ions.

Thus Townsend found that for hard X-rays,

$$\phi(NeZ) = \phi(Ne \overset{+}{2}Z)$$

for all values of Z , and so concluded that e ,⁺ the charge on a positive ion, is equal to twice e ,₋ the charge on a negative ion.

In the early stages of the experiment there was considerable difficulty in interpreting the results, as the average charge on the positively charged particles given off by the heated platinum seemed to vary from that given by radium to nearly twice this value, while the value given by the negatively charged particles seemed more constant and approximated to twice that given by the ions produced by the radium particles.

This seemed contrary to what one might naturally expect from a consideration of the fact that Townsend had found that the positive ions produced by Röntgen rays carried double charges under certain conditions but that negative ions from the same source did not.

Then the work of Richardson and Brown * with hot metals gave no indications of any ions from this source with double charges. Their experiments, however, did not determine the charge directly and all their measurements were made at low pressures, and this of course might make some difference.

Still an effort was made to see if there might not be some cause, such as a change in the rate of diffusion, for the variation in the ratio Q_r/Q_c other than an actual change in the charge.

I. It was thought that a variation of the size and position of the strip, causing unequal heating, might account for some part of the variation. However, on investigation this did not seem to give a solution, for the variations were as great when care was taken to keep these as constant as possible as when they were varied widely, and removing the heated strip to a greater distance did not decrease the variations.

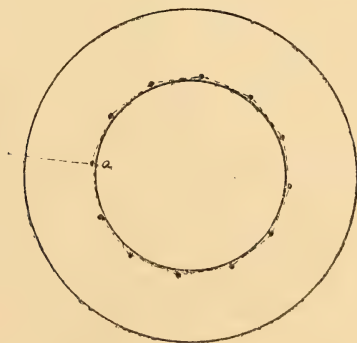
* Richardson & F. C. Brown, *loc. cit.*

II. It was suggested that perhaps unsteady air-currents were influencing the readings, but from the result above noted and from the fact that all the heating was from the top and that the only opening into the measuring-chamber (O, fig. 1) was small and symmetrically placed, it was concluded that this was hardly a possibility. This conclusion was confirmed by the next step.

III. The fact that the strip gave off considerable heat suggested that perhaps the chamber was being heated up, and that the variation in the apparent value of the charge was due to this change of temperature. Then during the early part of the time a strip was being used, the proportion of the charged particles going to the outer ring became gradually larger, indicating either a decrease in the charge, or an increase in the rate of diffusion, and thus lending colour to the above suggestion. However, the fact that this proportion always came to a fairly constant maximum value, and that there was no such variation when the negative ions were being tested, rather pointed the other way.

To test this the variation in the temperature in the chamber "K" was measured. The thermometer used consisted of fine platinum wire wound on hard rubber pins, which were screwed into holes drilled as near as possible to the inner edge of the central brass ring, as in figs. 1 and 2, in which the dotted line represents the wire. Fig. 1 gives vertical section; fig. 2 gives horizontal view of brass ring in question.

Fig. 2.



The middle of the wire was soldered to the brass ring at (a) so that it would not disturb the potential gradient appreciably.

The thermometer showed a maximum variation during a
Phil. Mag. S. 6. Vol. 23. No. 133. Jan. 1912. N

set of readings of less than 1° C.; but when, after the readings for Q_r/Q_c had reached a maximum and become steady, the temperature of the whole apparatus was raised about 4° C., there was no appreciable change in Q_r/Q_c . So the idea that the variation in Q_r/Q_c might be due to a change of temperature of the air in the chamber "K" was finally disposed of. The result seems to confirm the conclusion reached above—that the changes in Q_r/Q_c were not due to unsteady air-currents—for the outside heat was applied entirely from one side and would be much more likely to cause an uneven distribution of heat, and hence unsteady air-currents, than would the heated strip which was placed centrally above the testing-chamber.

IV. During the early experiments the strips of thin platinum were soldered directly to heavy copper connecting wires, but this was found to be unsatisfactory, as even when care was taken to use as little solder as possible, it fused with the platinum on being heated, and sometimes only three or four readings could be obtained from one strip. Then, doubtless, ionization was obtained from the solder as well as from the platinum. To avoid this the thin platinum was welded to thicker pieces of the same metal and the latter attached to the leads by small screw clips.

It is worth noting that the larger values of Q_r/Q_c corresponded roughly to the initial positive ionization and to the increased ionization at high temperatures. At first sight it might appear that the increased number of ions might have something to do with the change in Q_r/Q_c , but if this had any effect it would be due to the mutual repulsions between the ions, and this would be greater, and hence the spreading of the stream greater, when the ionization was strongest, but the opposite was the case, the number reaching the outer ring being greatest when the ionization was least. Then, too, no such effect was noticed when the ionization from RaBr was used, though the ionization was much greater than that from the hot platinum. Thus the conclusion that there was an actual change in the charges seemed inevitable, and efforts were made to get at the reason for this variation.

At first, when positive ions were being tested, the platinum was heated to a temperature only sufficiently high to produce these, but not high enough to give negative ions, and the temperature was increased only when it was desired to obtain the latter. Under these conditions it was found that the positive ions from a fresh strip carried an average charge nearly double that obtained with radium. While the strip

was being used this average charge at first gradually decreased, but after a few readings became fairly constant. If the strip after being heated for a time was left standing at the temperature of the room for a few hours, then on reheating some of the ions again carried double charges, though the average charge was smaller than with a fresh strip, and the strip came more quickly to a steady state where the average charge was not much higher than the charge on radium particles. (See Table I.)

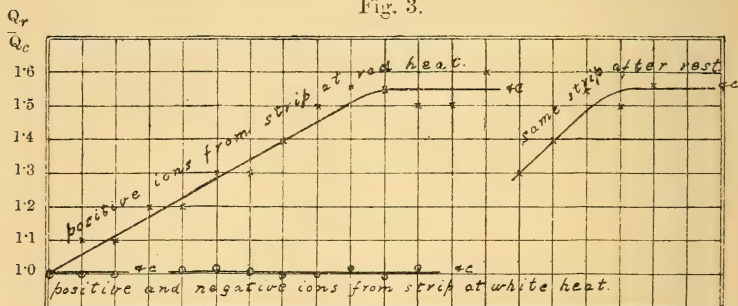
TABLE I.

Strip at bright red heat.		Strip at white heat.		RaBr.
100 V. pos.	100 V. pos.	100 V. pos.	60 V. pos.	100 V. pos.
1.0	Same strip after rest of 10 hrs.	1.05	1.85	1.7
1.1		1.05	1.7	1.6
1.1	1.3	1.05	1.65	1.8
1.2	1.4	&c.	1.7	neg.
1.2	1.55	neg.	neg.	1.7
1.3	1.5	1.1	1.7	1.7
1.3	1.56	1.15	1.6	1.6
1.4	&c.	1.1	1.9	1.8
1.5		1.0	1.8	1.8
1.56		1.0	&c.	
1.55		1.15	average charge about 1.7	
1.5		.97		
1.5		1.15		
1.6		&c.		
&c.				

In the table above is given the value of Q_r/Q_c from several strips under the conditions indicated. The first three sets of readings from two strips at 100 volts are shown graphically

in fig. 3. The charge is, of course, inversely proportional to the potential difference necessary to give the same value of Q_r/Q_c .

Fig. 3.



Thus it would seem that at a temperature only sufficiently high to give positive ionization, some of the ions from a fresh strip, or from one which had been resting in air, carry charges which are double the atomic charge; but when the strip is heated for a time a gradual change takes place, and as the large initial positive leak dies away a smaller and smaller proportion carry double charges, until a steady state is reached where the average charge is nearly equal to the atomic charge.

However, as noted above, no such change takes place with the negative ions, some of which at all times carry double charges. Then, too, when the positive ionization from a strip, heated to a sufficiently high temperature to give negative ions, was tested it was found that the average charge was about the same as for the negative ions. This result suggested that probably the negative ions also would carry single charges only, if obtained from a strip at a sufficiently low temperature. The apparatus as arranged did not admit of very low pressures being obtained, so hydrogen at atmospheric pressure was used and the strip heated in this.

As expected, the negative as well as positive ions carried single charges only when obtained from a strip at the lower temperature, and when this temperature was raised, both positive and negative ions carried some double charges. The proportion of these double charges to the whole number of ions rose gradually with the temperature of the strip just as with positive ions in air.

No attempt was made to measure the temperature of the strip, but keeping the same strip the heating current was varied from the smallest which would give positive ionization

to the greatest that it was thought that the strip would stand, and in taking the readings the current was gradually increased, and then lessened again to eliminate errors which might creep in from changes in the wire due to heating.

In the table below are given the differences of potential between the plates B and I which were found necessary to give the same value of Q_r/Q_c as 200 volts gave with the ionization from radium. The average results obtained from single strips are given, as combined results from different strips would have no meaning, because the same current with a different strip might mean quite a different temperature.

The numbers given for potential differences are of course inversely proportional to the average charge carried by the ions in question.

TABLE II.

Current.	P.D. to give constant Q_r/Q_c		Average charge.	
	Pos.	Neg.	Pos. *	Neg.
Strip "A" in air.				
12 amp.	205	no ions.	1	
14 "	120	"	1.7	
16 "	112	114	1.8	1.8
18 "	108	106	1.9	1.9
Strip "B" in air.				
14 amp.	193	no ions.		
In Hydrogen.				
12 amp.	203	no ions.	1	no ions.
14 "	191	180	1	1.1
16 "	184	172	1.1	1.1
18 "	112	90	1.8	2.2
RaBr in air.				
	200	200	1	1

It is probable also, although this was not tested, that at low pressures in air the same variations might be found.

A little work was done with positive ions from nichrome, which indicated that practically the same results might be looked for, but the experiments were not satisfactory. It was found impossible with the apparatus at hand to roll the

nichrome thin enough, and larger currents were necessary than could be carried for any great length of time by some of the leads in use. Then, too, it was found difficult to weld the nichrome and it was soldered to copper leads directly, with the same results as in the case of platinum, the solder fused with the nichrome so that but few readings could be obtained from one strip, and it was uncertain whether the ionization was due entirely to the nichrome or partly to the heated solder.

In the early stages of the experiment some doubt was felt as to whether these double charges might not be due to two ions, each with a single charge and each carrying along a load of air particles sticking together after being given off from the hot metal, and Millikan's * recent work did seem to make this worth considering. However, the fact that the number of these double charges depends entirely on the temperature of the strip and not at all on the temperature of the gas in the testing-chamber makes it seem highly improbable.

With the idea of confirming, or otherwise, these results some experiments on the velocity of ions from the same source were undertaken but are not yet ready for publication. This much, however, may be said. The maximum velocity was found not to vary with the temperature of the wire, but Rutherford † found that the average and minimum velocities decreased with increase in the temperature of the wire. This is in accord with the theory worked out by Wellisch ‡ if we assume that at high temperatures some of the ions carry charges $2e$ rather than e , for his theory would lead to the conclusion that a particle carrying a charge e would have a greater mobility than one carrying a charge $2e$.

In conclusion I want to express my thanks to Prof. O. W. Richardson for suggesting the experiment, and for the advice given me from time to time during its progress.

I wish also to thank Mr. C. Bol for advice and help with the mechanical details.

* R. A. Millikan and H. Fletcher, *Phil. Mag.* June 1911, p. 753.

† E. Rutherford, *Phys. Rev.* xiii. p. 321 (1901).

‡ E. M. Wellisch, *Phil. Trans. A*, vol. ccix. p. 249.

XV. *On the Rate of Evolution of Heat by Orangite.*

By HORACE H. POOLE*.

Outline of Method.

THE method employed is somewhat similar to that used for determining the heat evolution of pitchblende (Phil. Mag. Feb. 1910 & Jan. 1911) but differs from it considerably in detail, and resembles in principle that used by Pegram and Webb. The orangite in the form of lumps from 2 cm. diameter downwards is placed in a thick-walled airtight copper vessel which is then exhausted. The copper vessel is placed inside two Dewar vessels and the whole buried in ice. The difference of temperature between the copper vessel and the ice is measured by means of a multiple thermocouple. In the centre of the copper vessel is a coil of wire through which a small current can be passed, thus generating a known amount of heat inside the copper vessel, which, being a very good conductor, is sensibly at the same temperature throughout. Assuming that the difference of temperature between the copper vessel and the ice is proportional to the heat liberated in the former we can readily calculate the rate of generation of heat by the orangite by observing the ratio of the temperature differences with and without the electric heater.

Apparatus.

The general arrangement of the calorimeter is shown in the sketch (p. 184). A is the copper vessel whose walls are about 1.5 mm. thick, the joints being brazed. In the top is a circular hole about 2 cm. diameter through which the orangite was inserted. This hole was then closed by soldering on a brass cover plate in which is a valve consisting of a conical steel plunger which can be screwed down into a brass seating, thus closing a small hole leading to the interior of the copper vessel. This air-valve is the identical pattern employed by Dr. Joly in the gas globes used in his steam calorimeter, and was always found absolutely reliable. Down the centre of the vessel is a tube open at the top but closed at the bottom, in which the heating-coil is inserted.

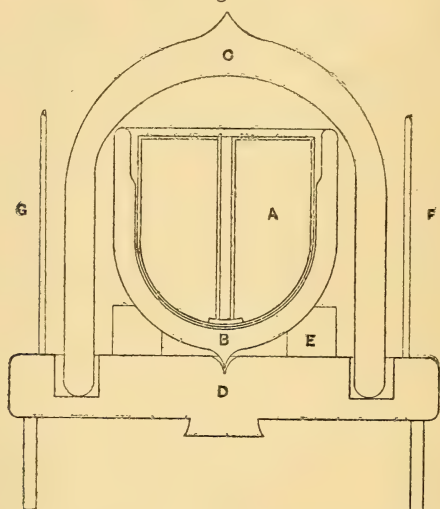
B and C are cup-shaped Dewar vessels, D is a circular wooden base soaked in molten paraffin wax and E a cork ring, also soaked in wax, which supports B. The annular groove in the base was filled with hot vaseline and C pressed down into it making a perfectly water-tight joint.

The thermocouple consists of 16 pairs of silk-insulated

* Communicated by the Author.

iron and nickel wires, .12 mm. and .15 mm. diameter respectively, soldered together at the junctions. The inner junctions are equally spaced round the rim of the copper

Fig. 1.



vessel in the space formed by the enlargement shown in the interior diameter of B. The junctions are kept apart and insulated from the copper by paper soaked in molten paraffin wax. In the space between the walls of B and C the wires are supported by a paper cylinder stiffened with paraffin wax. The idle parts of this annular space are filled with cotton-wool to lessen convection currents. The wires lead out through the vaseline under the rim of C, and the 16 outer junctions are enclosed in four glass tubes, two of which, F and G, are shown in the sketch. The four junctions in each tube are equally spaced along the tube so as to obtain the average temperature of the ice. Ordinary flexible leads are used and for about six feet are embedded in the ice, the arrangement of protecting tubes being the same as that described in a previous paper (Phil. Mag. Feb. 1910). The ends of the flexible leads are brought under the rim of C and soldered to a pair of iron wires of the couple, the connexions being close together under the bottom of B and inside the ring E.

For a description of the reversing key and galvanometer arrangements and of the system of ice vessels employed reference must be made to previous papers (Phil. Mag. Feb. 1910 and Jan. 1911).

The use of such a large number of junctions, although

not adding very greatly to the sensitiveness owing to the increased resistance, lessens the importance of small thermal effects at the galvanometer terminals. The resistance of the couple is 71.2 ohms, that of the galvanometer 30.0 ohms. As the thermo-electric power of the wires employed was found to be 31.94 microvolts per degree at 0° C., and the galvanometer is deflected on reversal 13.88 scale-divisions per microvolt applied to its terminals, we find that the deflexion per degree is $\frac{13.88 \times 31.94 \times 16 \times 30.0}{101.2} = 2,100$

scale-divisions. This figure is not needed in the determination but is useful in showing the order of the temperature differences involved.

The heating-coil is of german-silver wire, silk-insulated and wound on a thin copper rod. The coil just fits down the tube in the centre of A, and being a little shorter than the tube leaves a space about one centimetre long at the top, which is plugged with cotton-wool. The heater current is led in and out by flexible leads encased in rubber and copper tubes similar to those employed for the couple leads. The flexible leads terminate in the annular space between B and C, where they are connected to a pair of single insulated copper wires 0.195 mm. in diameter leading to the heating-coil. This arrangement lessens the conduction of heat along these leads. The total resistance of the heater and leads at 0° C is about 129.5 ohms. In view of the extraordinary results obtained this measurement was made several times so as to preclude the possibility of any error. It is estimated that the combined resistance of the flexible leads and the thin copper wires joining them to the heater must be about 0.4 ohm so that the resistance of the heating-coil must be about 129.1 ohms. The heater current is supplied by an accumulator. In the first series of experiments a single cell was used, its voltage being measured before and after each period of use on a Crompton potentiometer. In the second series two cells in series were employed, the voltage being read daily on a Weston voltmeter. As the resistance in series with the heater was never less than 2000 ohms the difference between the open circuit P.D. and the effective P.D. is negligible.

First Series of Experiments.

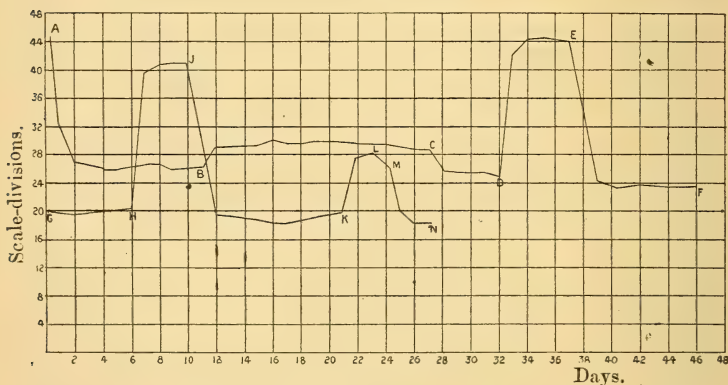
The orangite was put into the vessel and the valve-plate carefully soldered on. The vessel was then exhausted to a few mm. pressure by means of a Geryk pump, the temperature being kept between 65° and 75° C., and P₂O₅ tubes being inserted between the pump and the vessel. Having been kept at

this pressure for several days the vessel was finally exhausted as perfectly as possible by absorbing out the residual gas with coconut charcoal in liquid air. During this process some water was evolved by the orangite. The valve was then closed. The vessel contains 480.05 grams of orangite.

The ice used in this determination was specially frozen by an ice-making firm out of water which had been distilled in the laboratory. This ice was used for packing both the inner and the outer vessels, but for repacking the latter commercial ice was used. It was hoped that the use of this distilled-water ice would reduce the temperature variations which always occurred with commercial ice, but they remained as large as ever.

The daily temperatures are shown on the chart ABCDEF.

Fig. 2.



During the periods represented by AB, CD, and EF the heater was not in use. During the period BC current was flowing through the heater, 5000 ohms being inserted in series with it. As the voltage of the cell remained at 2.01 throughout the whole experiment the heater was generating

$$\left(\frac{2.01}{5129.5} \right)^2 \times \frac{129.1 \times 3600}{4.18} = .017 \text{ calorie per hour.}$$

During the period DE 2000 ohms were in series with the heater so that the heat generated was

$$\left(\frac{2.01}{2129.5} \right)^2 \times \frac{129.1 \times 3600}{4.18} = .0992 \text{ calorie per hour.}$$

The mean temperatures finally attained in the various periods are given in the table. In column A is the period,

column B gives the mean deflexion attained, C gives the heat generated electrically, D the increase in deflexion due to the heater obtained by subtracting the mean of the deflexions for the preceding and following period from the deflexion for the given period.

Column E is obtained by dividing C by D and hence gives the number of calories per hour necessary to cause a deflexion of one scale-division.

A.	B. Scale- divisions.	C. Calories per hour.	D. Scale- divisions.	E. Calories per hour.
AB	26.1	0		
BC	29.3	0.0170	3.65	0.00466
CD	25.25	0		
DE	44.3	0.0992	20.0	0.00496
EF	23.4	0		

The two figures in column E agree tolerably well, but as the rise for period BC was so small we may assign more weight to the value found for the period DE and assume that each scale-division corresponds to the emission of 0.0049 calorie per hour. It will be found that this value was confirmed by the later experiments.

Hence for the period AB the heat evolution per gram of orangite is found to be

$$\frac{26.1 \times 0.0049}{480.05} = 26.6 \times 10^{-5} \text{ calorie per hour,}$$

similarly for the periods CD and EF we obtain

$$25.8 \times 10^{-5} \quad \text{and} \quad 23.9 \times 10^{-5} \text{ calorie per hour}$$

respectively.

These values are extraordinarily high, being four times as high as the figures obtained for pitchblende. The diminution observed seemed to indicate that some temporary source of heat was in operation, so the whole calorimeter was laid aside unopened for nearly a year.

Second Series of Experiments.

Eleven months after the sealing up of the orangite a new determination was begun. For about a month various arrangements of the ice vessel were tried with a view to obtaining a more uniform temperature but as they were all failures the original arrangement was finally reverted to. During the month which immediately preceded the period

to which the chart GHJKLMN refers the calorimeter and its contents were kept approximately at 0° C.

During the periods GH, JK, and MN the heater was not in use. During HJ the resistance in series was 4000 ohms and the voltage of the battery measured on a Weston voltmeter was 4.03; these figures give a heat evolution of 0.106 calorie per hour.

During KL the resistance in series was 6000 ohms and the voltage 4.00, giving a heat evolution of 0.0475 calorie per hour.

On the day marked M the accumulator voltage was found to have suddenly fallen to 2.4, which explains the low reading observed. The heater was then turned off. In the following table the various columns have the same significance as before :—

A.	B. Scale- divisions.	C. Calories per hour.	D. Scale- divisions.	E. Calories per hour.
GH	19.75	0		
HJ	40.85	0.106	21.5	0.00493
JK	18.95			
KL	23.15	0.0475	9.55	0.00497
MN	18.3			

Unfortunately the period KL was unduly curtailed by the failure of the accumulator, and the experiment was brought to an end at N by the breaking of one of the wires of the couple (probably owing to a strain set up by some movement of the ice).

From this and the previous series there seems to be little doubt that each scale-division represents a generation of 0.0049 calorie per hour, so for the periods GH, JK, and MN the heat evolved by the orangite is 20.2×10^{-5} , 19.3×10^{-5} , and 18.7×10^{-5} calorie per hour per gram respectively.

These figures, while lower than the preceding ones, are still very much higher than was to be expected. The diminution also noticeable in these results is probably due to variations in the ice round the outer junctions. An exactly similar effect was often noticed with pitchblende when the calorimeter had been buried for a long time in the ice. The final period MN was so short that little weight attaches to it, and, as will be noticed, the lowest temperature recorded occurred in JK.

The calorimeter was finally opened and everything found in perfect order except for the broken wire. An attempt to connect the copper vessel to a pressure-gauge failed owing

to the valve having become stuck up, but on clearing out the valve air could plainly be heard rushing into the vessel, so that any leakage during the thirteen months for which the vessel was closed must have been small if not actually zero.

Sources of Error—Possible Effect of Air.

The internal volume of the copper vessel is about 220 cc. Of this at least 90 cc. must be occupied by the orangite, leaving an air-space of 130 cc. Let us assume as an extreme case that the valve leaked to such an extent that the air-pressure inside rose to that of the atmosphere (which it did not do). This would involve the entry of $130 \times 4.835 \times 10^{-6} = 6.3 \times 10^{-4}$ gram of water-vapour. Even if each gram of water yielded 840 calories, as much as it would do in combining with CaO, the heat so generated would only amount to 0.53 calorie. This quantity is entirely insignificant, as the results obtained indicate a generation of at least 900 calories during the time that the vessel was closed.

The oxygen entering the calorimeter would amount to 39 milligrams, a quantity which, even at the rate of 2000 calories per gram, would not seriously affect the result.

Uniformity of Temperature of Copper Vessel.

The heat generated by the heater must chiefly reach the walls of the vessel by conduction along the centre tube, which is about 0.7 cm. mean diameter, and is attached to the outer walls above and below. Let us assume that the heater is generating 0.1 calorie per hour, which is about the value generated on two occasions. Suppose half of this is set free at the upper end of the centre tube round a circle 0.7 cm. in diameter, and let us make the extreme assumption that heat only escapes from the vessel round the rim, which is about 7 cm. in diameter. Then for the radial flow of q calories per sec. across a disk of thickness t and conductivity K , we find that

$$\theta = \frac{q}{2\pi K t} \log_e \frac{r_2}{r_1},$$

where θ is the difference of temperature between two points distant r_1 and r_2 from the centre. In this case

$$q = 0.1 \div 3600, \quad t = 0.15, \quad K = 1 \text{ nearly, and } r_2/r_1 = 10,$$

so $\theta = 6.8 \times 10^{-5} \text{ }^\circ\text{C.}$

This is only about 0.15 scale-division, so it is evident that

serious differences of temperature cannot occur in the copper vessel.

Conduction of Heat along the Leads.

Two possible sources of error must be considered, namely, the possibility of heat entering the calorimeter by conduction along the leads of the couple and the heater, and the possibility that the heat-loss from the calorimeter is unduly augmented by conduction along the leads of the heater during the periods when the latter was heated by a current. As regards the first error, consider a very long wire of radius r_1 and conductivity k_1 encased in a protecting tube of radius r_2 and conductivity k_2 and buried in ice, one end being kept at a temperature θ_0 . If k_1 is large compared with k_2 the temperature will be sensibly uniform across any cross-section of the wire, and the flow of heat through the sheath will be approximately radial. With these assumptions we readily find that

$$\theta = \theta_0 e^{-\alpha x}$$

where

$$\alpha^2 = \frac{2k_2}{k_1 r_1^2 \log_e r_2/r_1},$$

θ being the temperature at a point distant x from the end. The actual leads consist of twin 35/40 "flex" enclosed in a single rubber tube. The total cross-section of the twin leads is approximately equal to that of a single wire 1 mm. in diameter, though the loss of heat to the ice, and consequently the fall of temperature with distance along the leads would evidently be more rapid from the twin leads. The external diameter of the thick-walled rubber tube encasing the leads is about 1 cm. If we assume

$$k_1 = 1, \quad k_2 = 3 \times 10^{-4},$$

we find for a wire 1 mm. in diameter $\alpha = 0.32$, hence for a point 30 cm. from the end θ is given by

$$\log_e \theta_0/\theta = 30 \times 0.32 = 9.6, \quad \text{or} \quad \theta_0/\theta = 15,000 \text{ about,}$$

so if

$$\theta_0 = 15^\circ \text{ C.}, \quad \theta = .001^\circ \text{ C.}$$

As several feet of the leads is buried in the ice, and part of this length is enclosed in copper tubes to facilitate the radial flow of heat, it is evident that the leads near the calorimeter must be exceedingly near zero and far below the temperature of the calorimeter.

As the ice in the outer vessel melted, the length of leads buried in the ice decreased, but on repacking the outer vessel

no regular change in the deflexion was noted, the fluctuations that occurred being apparently independent of the repackings. This is also an argument against the entry of heat into the calorimeter through air-cavities or conduction along the wooden legs.

As regards the possible loss of heat along the heater leads, these are each 0.195 mm. in diameter and 15 cm. long from the heater-coil to the junction, with the flexible leads in the annular space between the inner and outer Dewar vessels. Assuming that the conductivity of copper is unity, we find that for a difference of temperature of 1° C. between the ends of the leads the flow along the pair is only 0.144 calorie per hour, so for the actual temperature differences involved the flow would be negligible. Moreover, the heating-coil, even when in use, must be at very nearly the same temperature as the rest of the copper vessel, so there is no reason why the heat generated electrically should escape more readily than that produced by the orangite.

It is possible that the heat-loss may be slightly augmented during the periods that the heater is in use by increased evaporation from the cotton-wool used to plug the mouth of the heater-tube. This probably contains some moisture and may be raised slightly above the temperature of the rest of the copper vessel by the action of the heater. As, however, the evaporated water could only condense on the inner surface of the outer Dewar vessel, it is hard to see how any relatively important increase in the heat-loss could occur in this way,

Conclusion.

The apparent decrease in activity observed in the second series of experiments is probably spurious, as the rate of decrease is much greater than that obtained by comparing the first and second series. It is probably due to irregularities in the ice temperature, as already suggested. The mean evolution of heat in the first series is 25.4×10^{-5} , and in the second 19.4×10^{-5} calorie per hour per gram. There seems to be little doubt that this heat must be generated by the orangite. The orangite is from Arendal, Norway, and an estimation by the radioactive method indicated the presence of 36 per cent. of elemental thorium. Now Pegram and Webb obtained a value 2.1×10^{-5} calorie per hour per gram of thorium oxide in radioactive equilibrium, and this value is much more nearly in accordance with radioactive theory than the very large values obtained in the present experiments.

The only possible explanation appears to be that the

orangite may be undergoing some molecular or chemical change. The mineral is subject to alteration, and perhaps the warming and loss of water during exhaustion started some change which was still proceeding at only a slightly decreased rate a year later. As the total heat evolved during that time only amounts to about 2 calories per gram of orangite it might possibly be produced in this way, though the smallness of the diminution observed in the rate of evolution indicates that the action will proceed for several years to come, and by the time it is over the quantity of heat generated by each gram may amount to a much larger figure.

It is hoped to make a fresh determination on an entirely fresh sample of orangite which will not be heated beforehand, and also to employ the method used with pitchblende as a check on the values obtained above.

In conclusion I wish to express my gratitude to Dr. Joly for his kind assistance and advice throughout the work, and for the loan of the orangite employed.

Physical Laboratory,
Trinity College, Dublin,
October 5, 1911.

XVI. *The Ionization produced by Carbon at High Temperatures.* By J. N. PRING, D.Sc., and A. PARKER, University of Manchester*.

THE escape of negative electricity from heated carbon was noticed by Edison† when making experiments with lamp filaments. This leak of current from a heated filament to an adjacent electrode which is at a positive potential relative to the filament can, in some cases, become of the same order as that conducted through the filament. Edison found that when these filaments have been used for some time the ionization effect diminishes, but increases again if the carbon is allowed to stand.

O. W. Richardson‡ made systematic measurements of the ionization produced by carbon. Use was made of a carbon filament and a surrounding metal cylinder, and between these a potential difference varying from 30 to 300 volts was maintained, the heated carbon being made negative. The current produced by ionization was conducted across to the surrounding metal. By exhausting to very low pressures,

* Communicated by Prof. E. Rutherford, F.R.S.

† Engineering (1884), p. 553.

‡ Phil. Trans. (1903) A. cci. p. 497.

from 0.1 to 0.001 mm. the influence of the ionization of the surrounding gas was supposed to be eliminated, and the currents produced were considered to be due to the liberation of corpuscles from the carbon.

It had previously been stated by M'Clelland * that the negative ionization from metals is independent of the pressure over a range from 0.04 to 0.004 mm. The ionization currents found by Richardson, and attributed to the liberation of corpuscles, ranged from 10^{-8} to 2 amps. per square cm. of carbon, according to the temperature. A formula which had been deduced to show the relation between ionization and temperature was found to be in good agreement with the

experimental results. In this equation $I = A\theta^{\frac{1}{2}} e^{-\frac{b}{\theta}}$ where I denotes the ionization, A and b are constants, and θ is the absolute temperature. In the case of carbon, Richardson found that $A = 10^{34}$ and $b = 9.5 \times 10^4$. According to this formula, the ionization will increase at a rate which at 1500° is about equal to the 50th power of the temperature. As is well known, there are no means of precisely estimating the temperature of thin filaments.

F. Deiningering † investigated the ionization from carbon and various metals alone, and in presence of lime, and concluded that Richardson's formula applied in every case up to 1450° . Thus $\log I - \frac{1}{2} \log \theta$ was plotted against $\frac{1}{\theta} 10^4$, and found to give a straight line. No mention is made of the pressure.

H. A. Wilson ‡ investigated the ionization from platinum and found that this varied very much with the previous treatment of the metal. Thus, by long continued heating, or else by previously submitting to the action of nitric acid, the ionization was largely diminished. He concluded that the ionization from platinum is independent of the pressure from 0.2 to 0.001 mm., but that a reduction to $\frac{1}{250,000}$ of the original ionization is produced by removing the last traces of occluded hydrogen. Wilson states that in some experiments carried out with carbon he confirmed the general results of Richardson.

The present work was undertaken with a view to examine the ionization from carbon at temperatures which were more

* Proc. Cambr. Phil. Soc. x. p. 241; xi. p. 299.

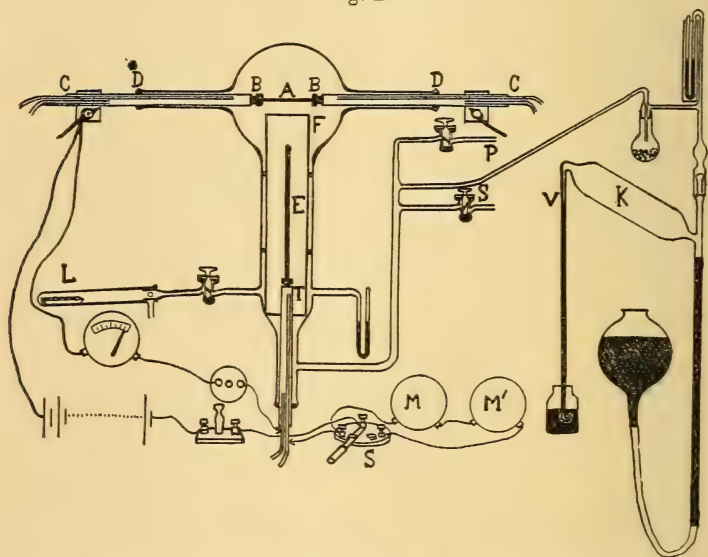
† *Ber. deutsch. physik. Gesell.* (1907) ix. p. 674.

‡ Phil. Trans. (1904) A. ccii. p. 243.

accurately measured than in previous work, to extend these up to about 2000° , and, at the same time, to notice what influence is exerted by the pressure of the surrounding gas and the condition of the carbon. No attention seems to have been paid by previous workers to the chemical purity of the carbon.

The apparatus used in the present work (fig. 1) was

Fig. 1.



designed primarily for examining the phenomena at the anode during the discharge with high currents, and consisted of a tubular glass flask, in which a carbon rod (A) was supported by inserting in the graphite plugs B, B, which themselves were soldered into the water-cooled brass tubes C, C. An air-tight joint was made at D, D, by means of soft wax. The water-cooled tubes served for leading in the current which was used to heat the carbon. The carbon rod used was 5.1 cm. long and 0.50 mm. diameter, or 8.01 sq. cm. surface. This arrangement of the apparatus enabled the rod to be heated to 2200° .

Temperature Readings.—Accurate temperature readings were taken with a Wanner optical pyrometer. This was directly calibrated against a standardised thermocouple up to 1400° , and at the "black body" melting-point of platinum, 1545° *, and as carbon has been found to radiate approximately as a "black body," the temperature readings will

* Holborn and Henning, *Sitzungsber. k. Acad. Wiss. Berlin* (1905) xii. p. 311.

follow closely the platinum scale. The small amount of absorption through the glass vessel was allowed for in all cases where direct temperature readings were taken. This absorption was estimated by heating a strip of platinum with a constant current and reading the temperature optically, firstly by sighting directly on the surface, and secondly by allowing the light to pass through the globe. In some of the latter measurements, after the resistance of the carbon had become constant through graphitization, the relation between temperature and current through the rod was found and made use of for the temperature estimations when the vessel had, after prolonged use, become coated with a rather opaque film of carbon. The accuracy of the temperature readings can probably be relied upon to within 35° at 1500° on the platinum scale and 75° at 2000° on the optical scale.

For the anode, a graphite rod (E) was soldered into the water-cooled brass tube (T), the top being placed at 4.8 cm. distance from the carbon (A). During the experiment, a large difference of potential (usually 330 volts) was maintained between E and A; the high-potential circuit being connected through the galvanometers M and M' which were of different ranges, one giving a deflexion of one scale-division for 4.1×10^{-9} amp. and the other of one division for 6×10^{-7} amp. For higher currents these were replaced by a milliammeter reading to 0.5 amp. and for measuring currents during discharge an ammeter reading to 30 amps. was used. By means of the two-way switch S the galvanometers were thrown out of circuit except during the moment when readings were being taken.

Exhaustion of Apparatus.—In the early experiments use was made of lithium for reducing the pressure. For this purpose the metal was placed in an iron boat contained in a tube of Jena glass (L). By surrounding this tube by an electrical furnace, and using a thermo-junction pyrometer, it was found that beginning with low pressures absorption of the gas to within one per cent. of the volume took place at 450° , though at this temperature the lithium very slowly sublimed and gradually reacted with, and finally cracked, the glass. The exhaustion was afterwards effected with an automatic Sprengel pump connected to P, which would reduce the pressure to 0.0001 mm. when the apparatus was cold. The Töpler pump K (not drawn to scale), the volume of which was $\frac{1}{5}$ that of the whole apparatus, was also used for evacuating, and as a McLeod gauge for measuring the pressure. For this latter purpose the volume of gas in K was compressed in the capillary, of known volume, and the

length of this tube occupied by the gas when at 5 cm. pressure was measured. The tap at P leading to the Sprengel pump was turned off for a short time before each reading of the pressure. The estimations of the pressure in this work were of course subject to the same limitations that apply in all cases where use is made of the McLeod gauge, through the presence of condensible gases and surface condensation on glass.

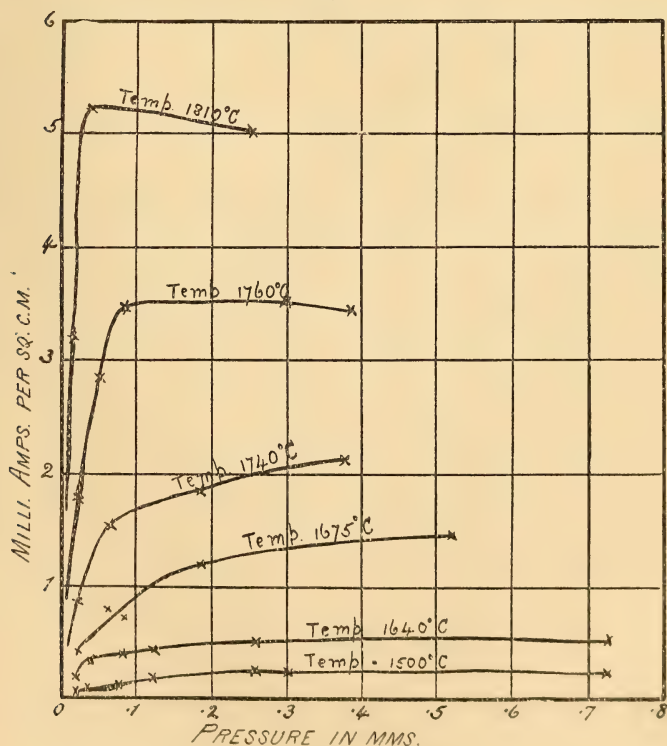
Purification of Carbon.—The carbon used consisted of amorphous retort carbon and contained about 2·5 per cent. ash (oxides of iron, silicon, &c.), and 0·2 per cent. of combined hydrogen. The method of purification employed consisted in heating for long intervals at temperatures varying from 1700° to 2000°, and maintaining very low pressures. In this way impurities are gradually volatilized away and occluded gases expelled. It has never been found possible to purify carbon completely*, on account of the tenacity with which it holds many elements in large quantities at temperatures greatly above their points of volatilization. (After use in the experiments below, the carbon was analysed by combustion in oxygen and found to contain 0·091 per cent. of ash.) The graphite rod E was occasionally heated during the above treatment by causing a discharge to pass between this and the heated carbon rod. Suitable conditions of temperature of the rod and pressure were arranged, and a potential difference of about 250 to 350 volts was applied between the carbon and the graphite. When the discharge was once started, a voltage of 40 to 60 was sufficient to maintain a current of 20 to 30 amperes, and the graphite was gradually raised to a bright white heat at the end, and the inside glass cylinder (F) to the softening point. After heating the carbon rod in this manner for some 20 to 30 hours it was found possible, at any time when the apparatus was cold, to reduce the pressure in the vessel to 0·0001 mm. within 2 hours. On raising the temperature of the rod, however, the pressure always rose immediately, and amounted to about 0·01 mm. when at 1800°. This could not be reduced any further by long continued heating and exhausting. After the globe had become coated with a thin film of carbon, the pressures obtained when the rod was heated were higher than before, and for a given temperature of the rod remained constant, even after heating and pumping for several days. This residual gas is probably due either to carbon monoxide which would be formed by reaction between the oxides of the glass and the deposited film of

* Cf. Pring, Trans. Chem. Soc. (1910) xcvii. p. 504.

carbon, a reaction which would proceed to a certain equilibrium value at any given temperature, or else it is due to oxygen resulting from slight dissociation of the oxides in the glass, though the temperature of the latter, of course, never reached the softening point.

Measurement of Ionization.—A potential difference of about 330 volts was applied between E and A (fig. 1) except where otherwise stated, and the latter made negative. In this way it was hoped to collect most of the ions coming from the carbon. At this voltage, however, the original ionization must have been increased by collision, as only about half the current was obtained on using 200 volts. It was found that by placing the graphite rod E at 11 cm. instead of 4.8 cm. from the carbon, a fall in the ionization current of not more than one-fifth was caused. The results obtained when using impure carbon are shown in the form

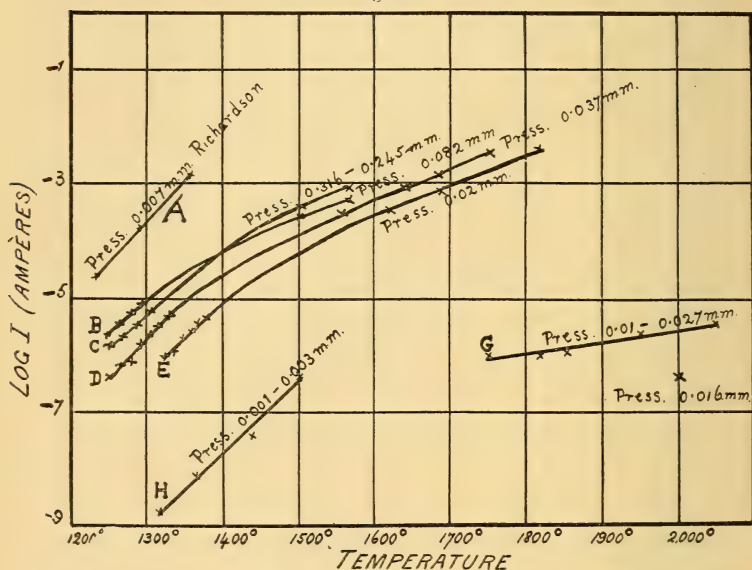
Fig. 2.



of curves in fig. 2, where the ordinates denote the ionization current in milliamperes per 1 sq. cm. surface of carbon and

the abscissæ, the pressures. In fig. 3 are seen the results of another series of experiments which were extended to much

Fig. 3.



lower pressures, and where a higher degree of purity of the carbon was obtained. In this diagram the ordinates denote the logarithm of the ionization currents (in amperes) for one square cm. of cathode surface, and the abscissæ, the temperatures. The results obtained by Richardson are shown in this diagram at A. In the present work it was found that the minimum of ionization is not obtained at the pressures used by Richardson, but that the values fall continuously with diminution of pressure and with continued use of the same carbon as it becomes progressively purer. Beginning with higher pressures and unpurified carbon, it was found that the maximum ionization current is obtained at about 0.1 mm. pressure and that the values are about one-tenth those given by Richardson as the minimum for the same temperature. The values at 0.001 mm. were about $\frac{1}{50}$ those at 0.1 mm. In the experiments at higher pressures with impure carbon, shown in curves B to E, at temperatures between 1250° and 1820°, if the values of $\log I - \frac{1}{2} \log \theta$ are plotted against $\frac{1}{\theta} 10^4$, a straight line is obtained; but at higher temperatures, which were taken up to 2050°, and lower pressures, the ionization increased with the temperature far less than is required by Richardson's formula, and

varied very much with the condition of the carbon. Curves B to E were carried out with impure carbon, and G and H after heating at temperatures between 1500° and 2100° and pressure between 0.005 and 0.05 mm. for a total period of about 40 hours. The values obtained in G and H, as typical experiments, are given in the table below.

G.				
Amps. through rod.	Temp.	Field (volts).	Ionization, amperes per sq. cm. cathode.	Pressure in mm.
80	1750°	200	8.0×10^{-6}	0.010
85	1810°	"	8.6×10^{-6}	0.021
90	1850°	"	10.6×10^{-6}	0.010
100	1950°	"	16.0×10^{-6}	0.020
110	2050°	"	16.0×10^{-6}	0.027
H.				
40	1250°	330		0.001
45	1315°	"	1.23×10^{-8}	0.001
50	1370°	"	6.17×10^{-8}	0.001
55	1440°	"	3.29×10^{-7}	0.002
60	1500°	"	4.0×10^{-6}	0.003

In results G when 110 amperes was applied, a discharge suddenly occurred, 20 amperes passing through and the voltage across the terminals falling to 50. At these low pressures the discharge began abruptly from the smallest ionization current. Its formation was always very uncertain, and at higher pressures, 0.05 to 0.2 mm., it generally occurred at lower temperatures (*i. e.* 1550° to 1850°) and was preceded by a bright glow in the whole space of the flask, or else by blue striations, accompanied by currents up to 0.5 ampere.

In experiments in which at the low pressures the small ionization current was obtained, it was found that on admitting a small quantity of air to the apparatus the current immediately rose to values similar to those shown in curves B to E. There was no measurable positive ionization produced from the carbon, up to 2000°, when the field (of 200 volts) was reversed.

Summary.

Measurements were made of the ionization produced by heated carbon at definitely known temperatures between 1300° and 2050°, and at various pressures.

The negative ionization from heated carbon was found to fall continuously, both with reduction of the pressure and with progressive purification of the carbon.

The lowest value found at 1300° , with a potential difference of 330 volts, was 1.5×10^{-9} ampere per square cm. surface of carbon, whereas Richardson found at this temperature 1.3×10^{-4} . At 2000° with a potential difference of 200 volts, the lowest value found was 4×10^{-7} ampere, while Richardson's formula gives, at this temperature, about 100,000 amperes.

Above 1800° the ionization only increased very slightly with the temperature.

These results clearly show that the large currents hitherto obtained with heated carbon cannot be ascribed to the emission of electrons from carbon itself, but that they are probably due to some reaction at high temperatures between the carbon or contained impurities and the surrounding gases which involves the emission of electrons.

We are deeply indebted to Prof. Rutherford and Dr. H. Geiger for much valuable advice during the course of this work.

Physical Laboratories,
Victoria University,
Manchester.

Addendum.

Effects similar to the above results obtained with carbon have been noticed by Soddy* in the case of the Wehnelt lime cathode. It was found that, at very low pressures, this cathode ceased to produce ions, whereas, according to previous experimenters, greater saturation currents were given the lower the pressure. Soddy concludes that electronic emission can only account for a negligible fraction of the total current, the remainder being carried by the residual gas.

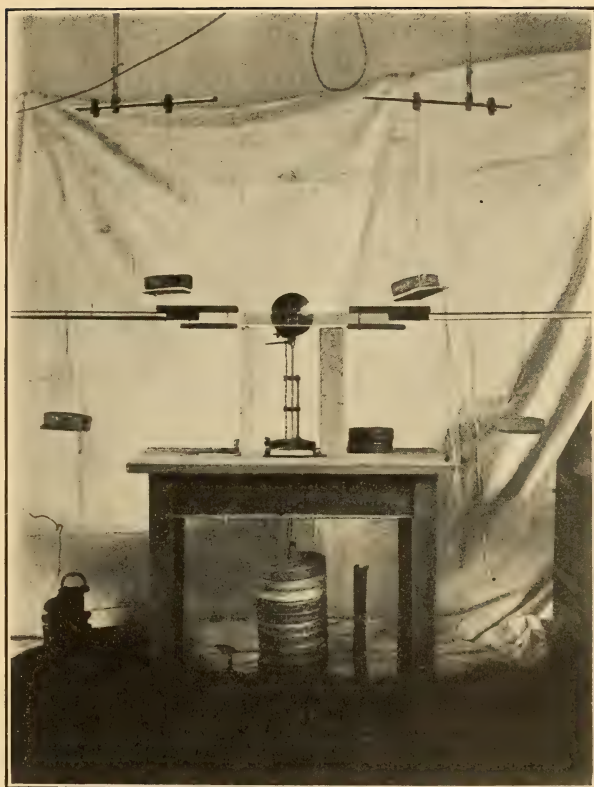
Richardson† reaffirms the opinion that the negative leak from hot platinum is independent of the pressure at low pressures, and that these gases "only appear to increase the fundamental electronic discharge from the hot cathode by a process involving the occurrence of ionization by collisions."

Wehnelt‡ also contradicts the above inference of Soddy, and states that in the best possible vacuum the total current is sustained by the electrons emitted from the glowing oxides, and indeed at all pressures below about 0.1 mm.

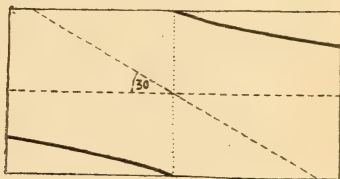
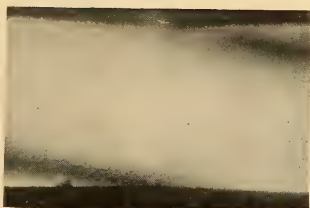
* 'Nature,' lxxvii. p. 53 (1907).

† 'Nature,' lxxvii. p. 197 (1907).

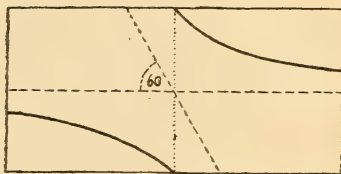
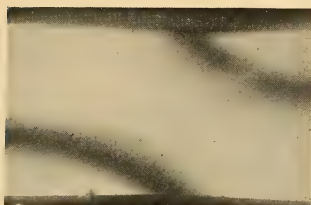
‡ *Phys. Zeitschr.* ix. p. 134 (1908).



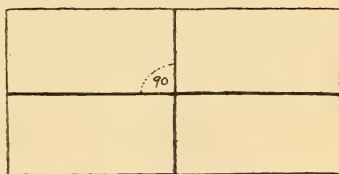
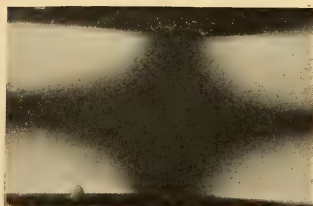
$i=15^\circ$.



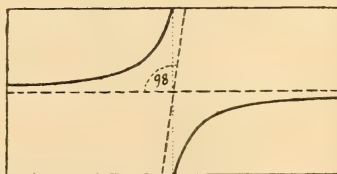
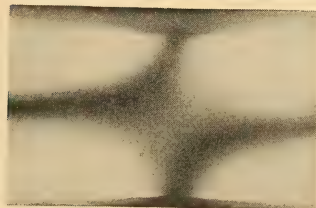
$i=30^\circ$.



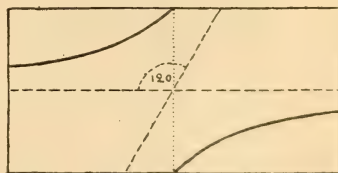
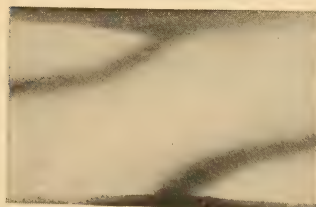
$i=45^\circ$.



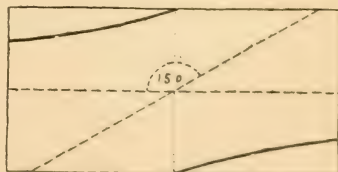
$i=49^\circ$.



$i=60^\circ$.



$i=75^\circ$.



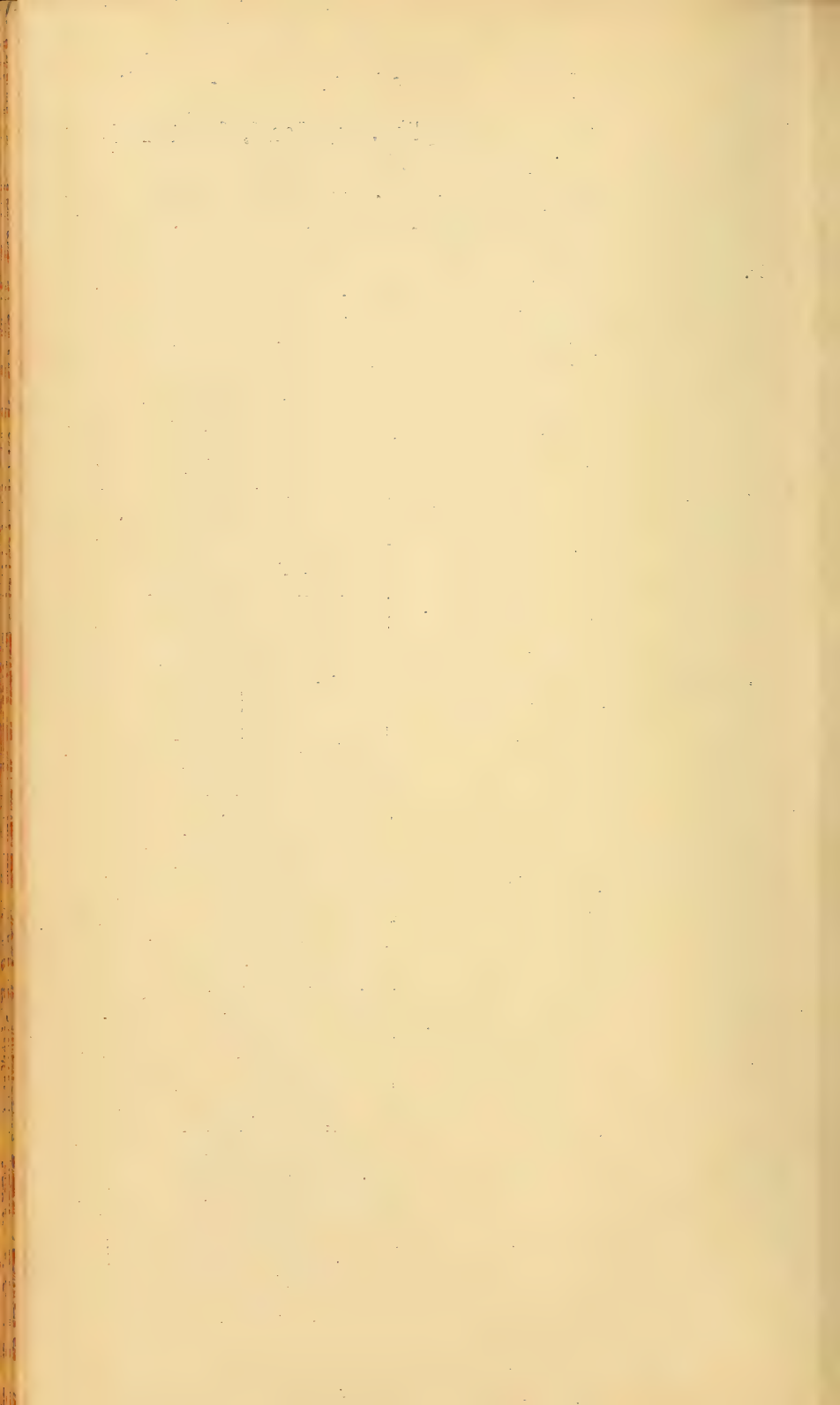


FIG. 1.

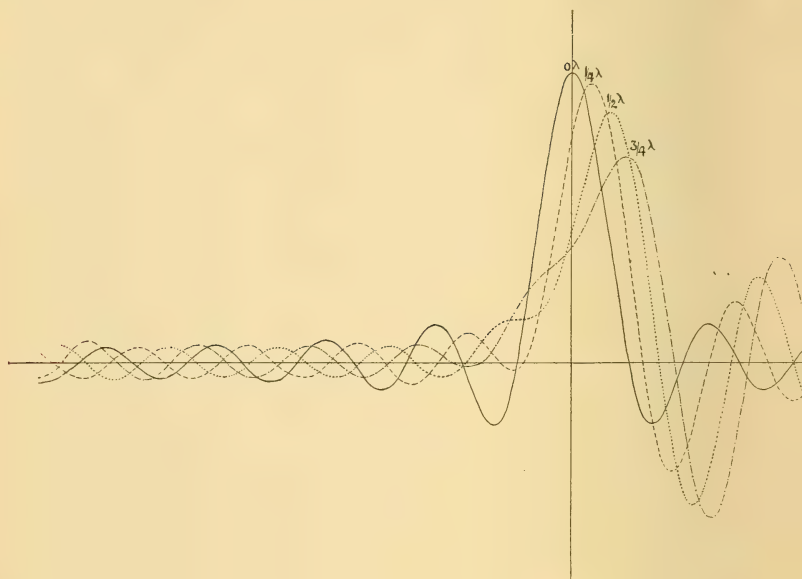
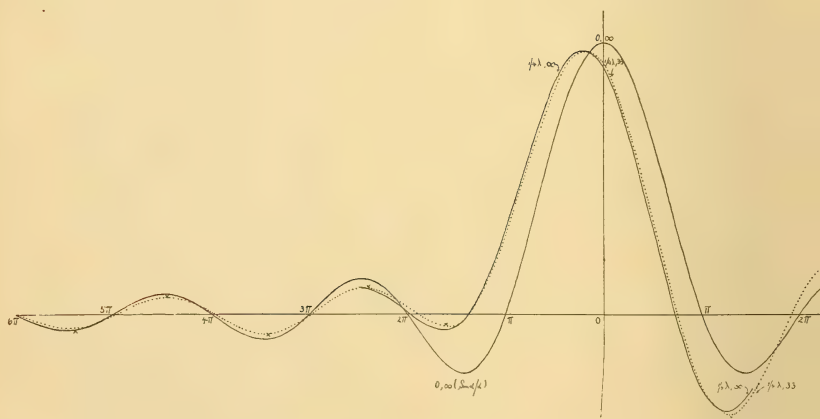
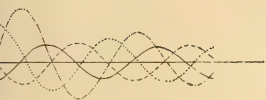
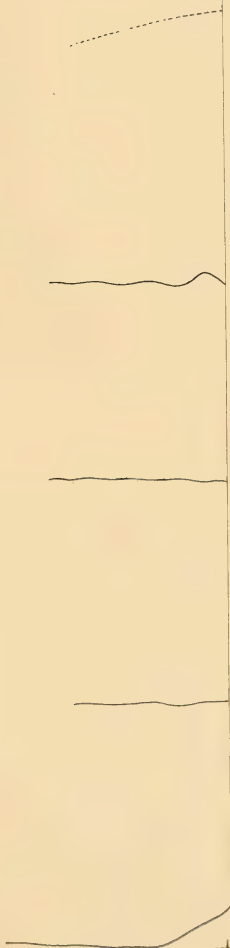
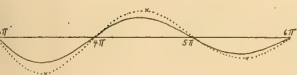


FIG. 3.





$0, \infty$ ($\sin \alpha / \lambda$) ———
 $\frac{1}{2}\lambda, \infty$ (Rayleigh) ———
 $\frac{1}{2}\lambda, 33$
 $\frac{1}{2}\lambda, 19$ x x x



RATION IN DIFFRACTION SPECTRA.

FIG. 1.

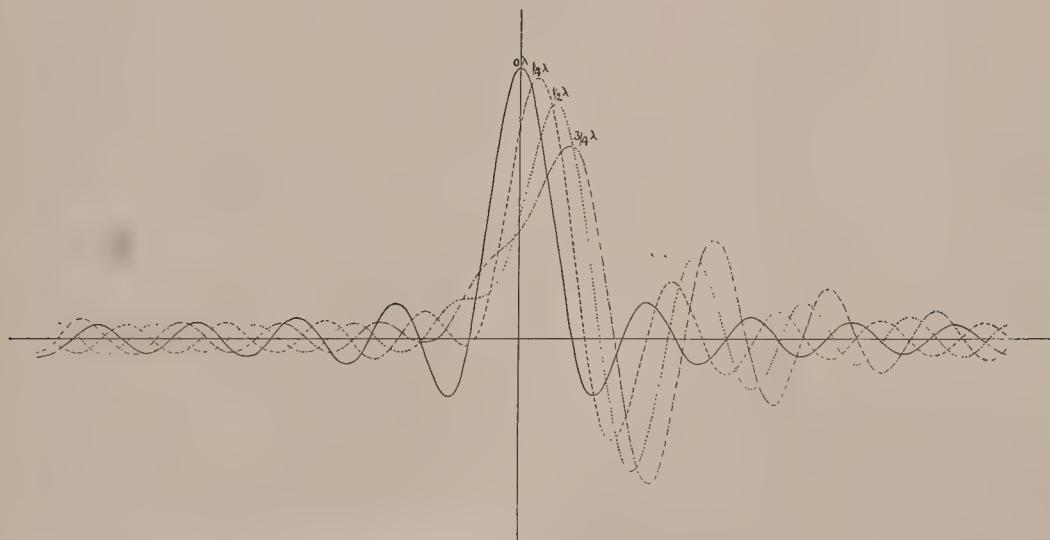


FIG. 3.

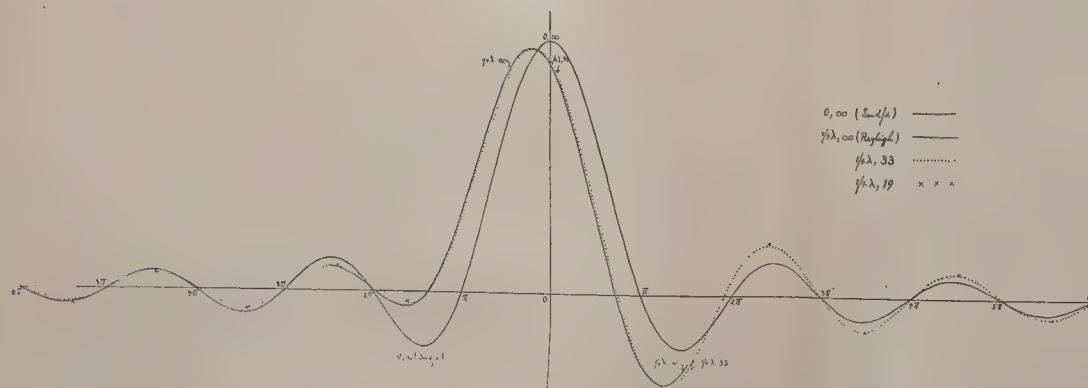
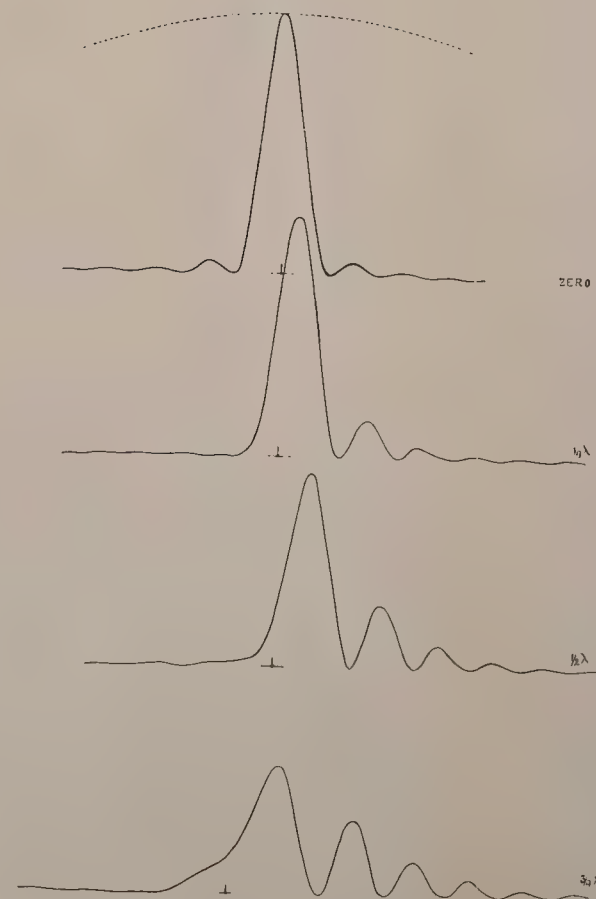
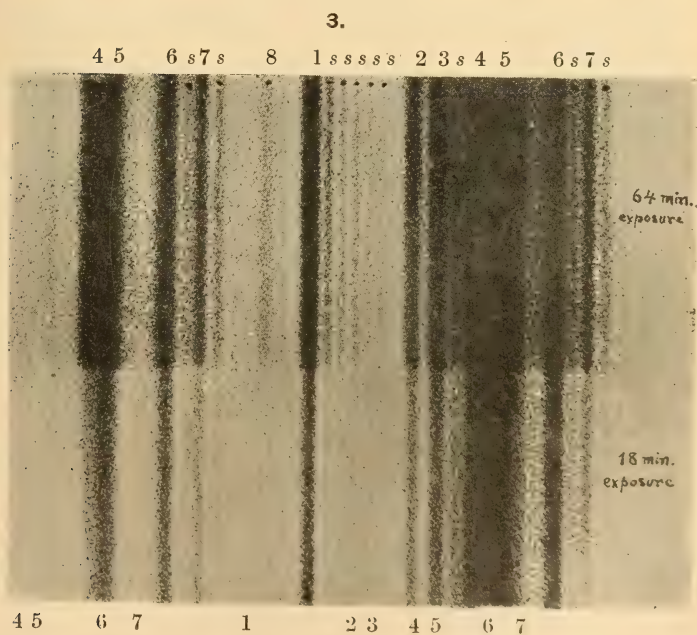
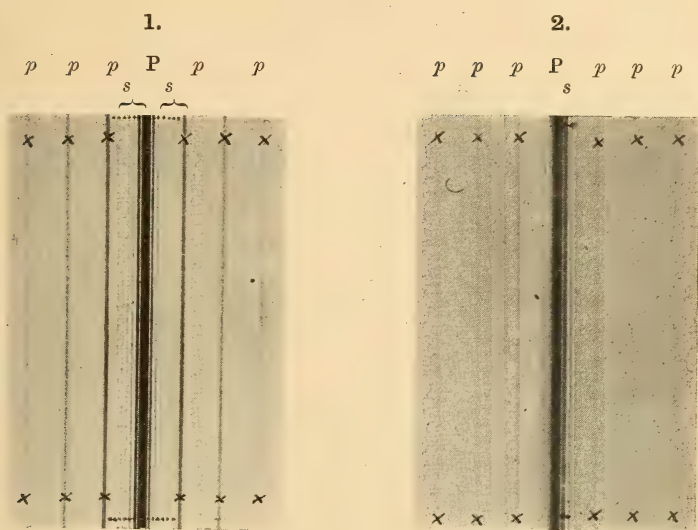


FIG. 2.



ABERRATION IN DIFFRACTION SPECTRA.

17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100



Green Mercury Line, 5461 Å.

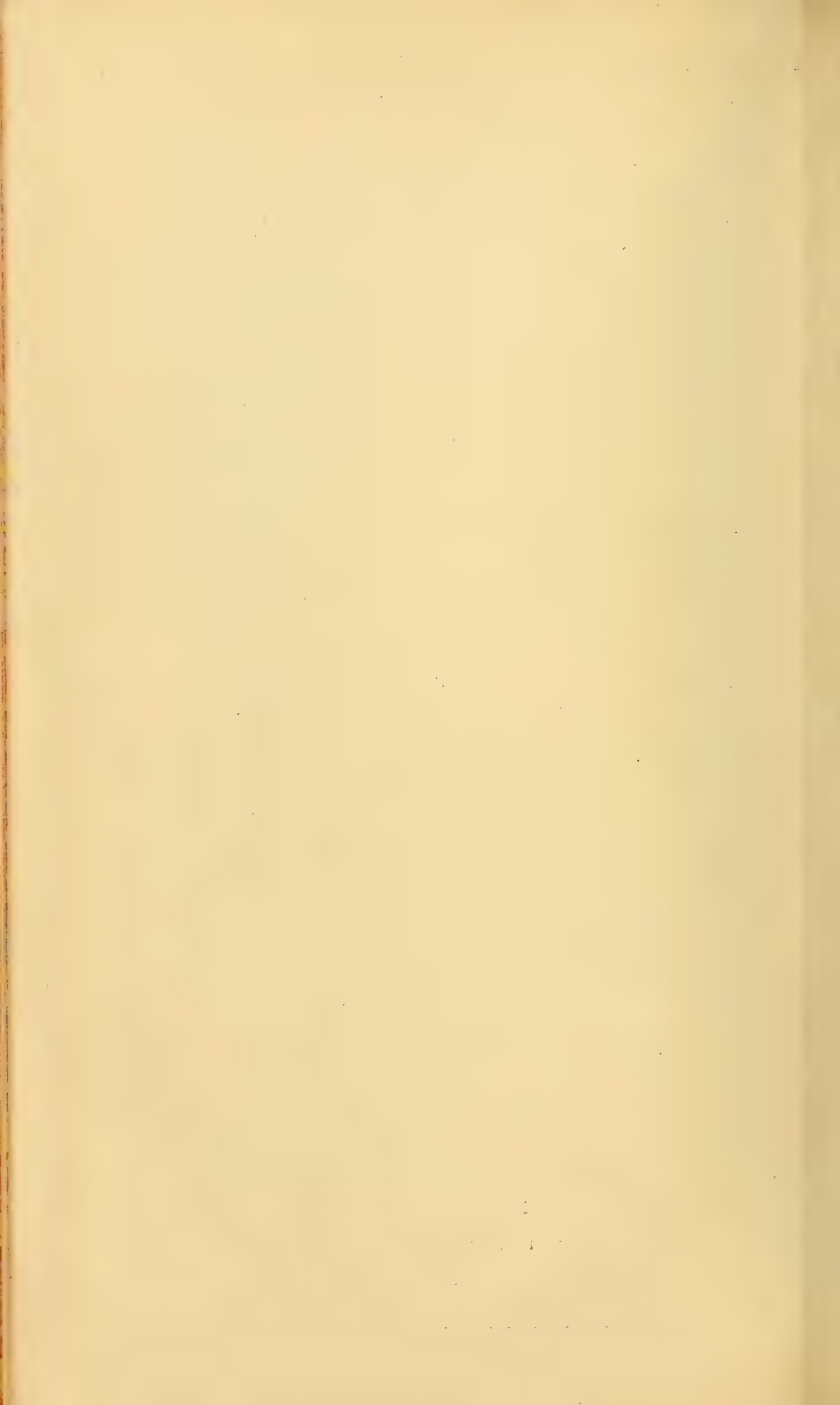
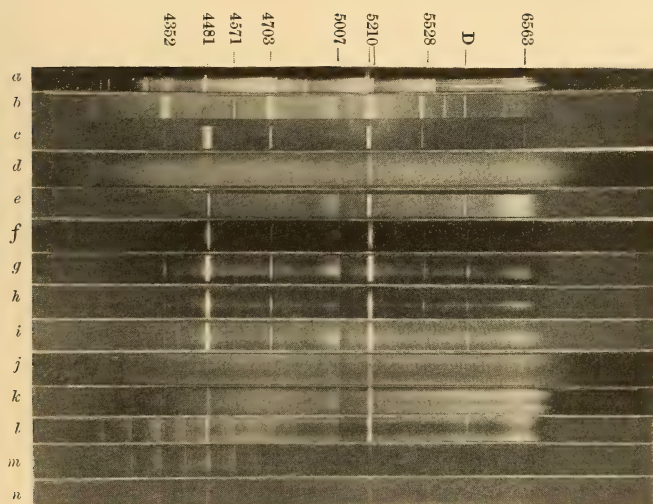


FIG. 2.



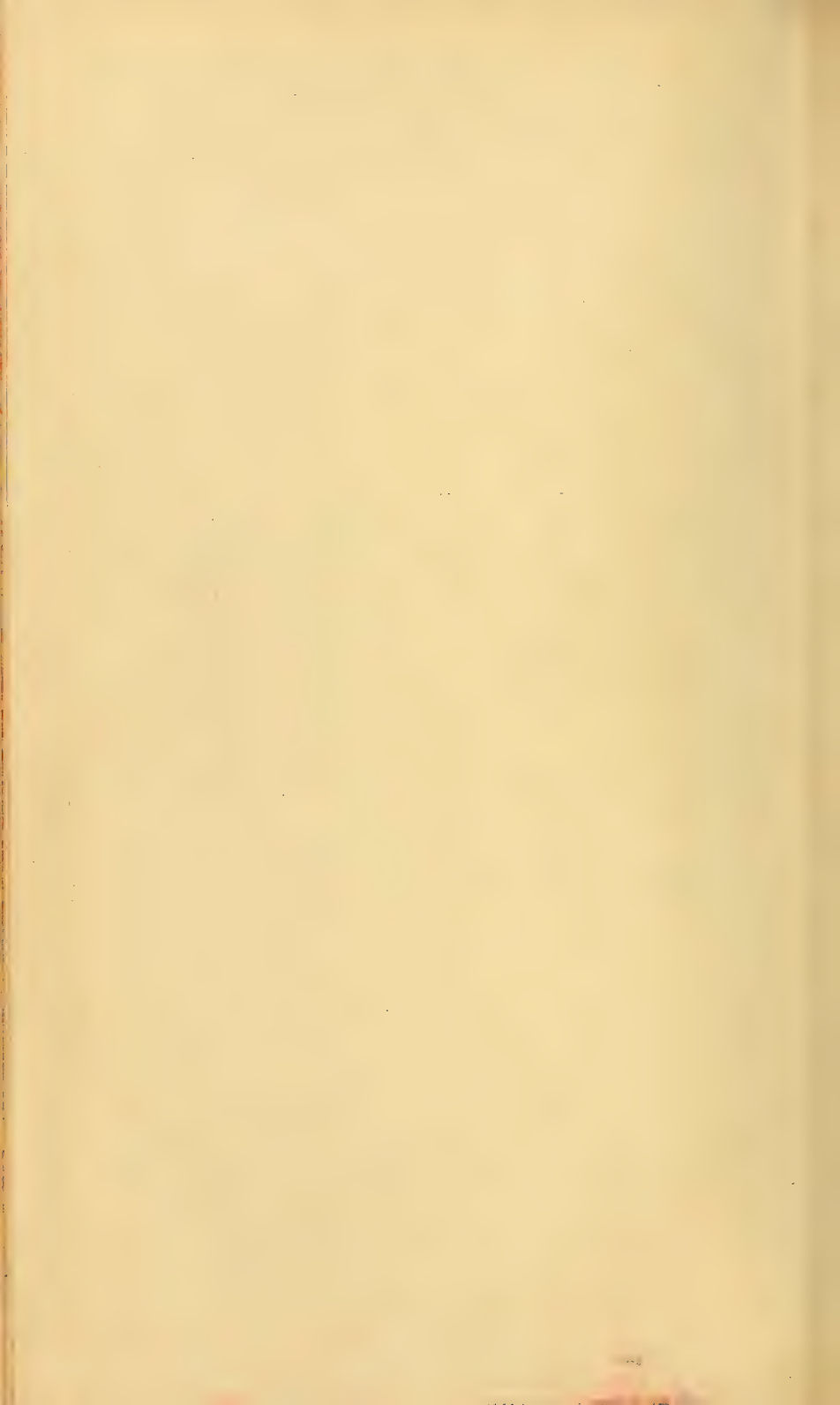






FIG. 1.—Uncharged.



FIG. 2.—Charged.



FIG. 3.—Uncharged.



FIG. 4.—Uncharged.



FIG. 5.—Charged,
160 Volts.



FIG. 6.—Charged,
240 Volts.



FIG. 7.—Charged,
720 Volts.



8a.
Uncharged.

8b.
Charged,
80 Volts.

8c.
Charged,
720 Volts.

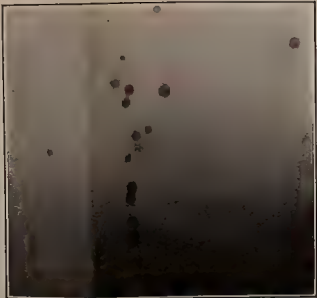


FIG. 9 a.—Uncharged



FIG. 9 b.—Charged,
80 Volts.



FIG. 9 c.—Charged,
720 Volts.



FIG. 10 a.—Charged,
240 Volts.



FIG. 10 b.—Charged,
720 Volts.

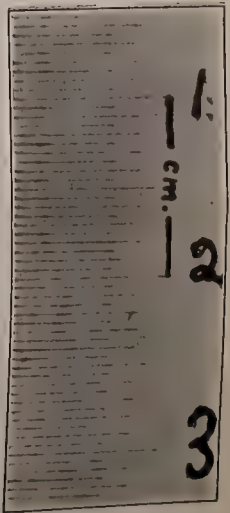


FIG. 11.



THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

FEBRUARY 1912.

XVII. *The Radioactivity of the Rocks of the St. Gothard Tunnel.* By J. JOLY, F.R.S.*

IN 1908, in the course of a Presidential Address to Section C of the British Association, I gave a summary of the results of my experiments on the radium content of certain rocks from the St. Gothard tunnel. These results showed considerably greater amounts of radium in the granite at the northern end than elsewhere throughout the length of the tunnel.

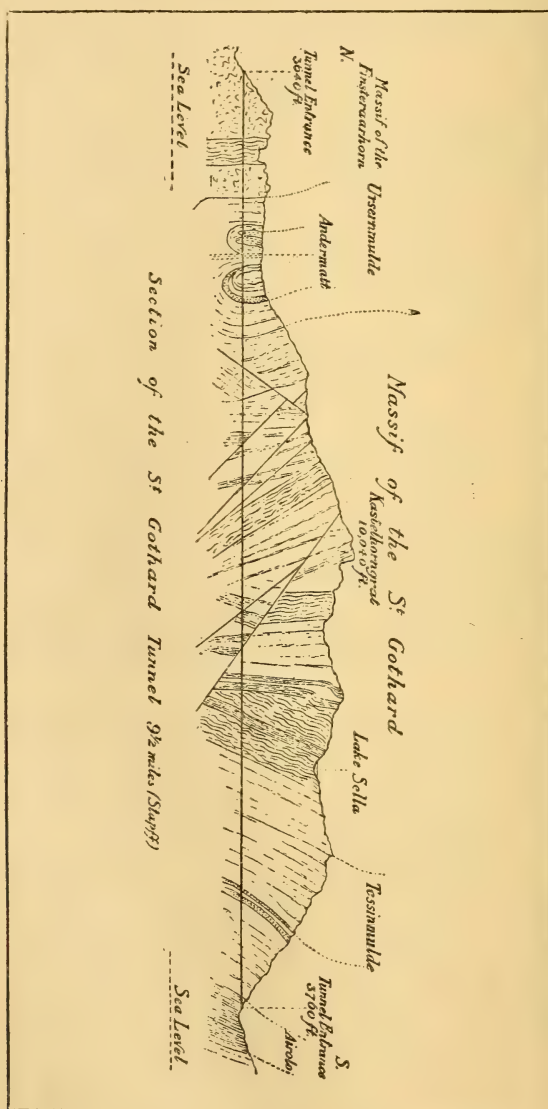
The accompanying section (after Stapff) shows the general geological structure of the range through which the tunnel passes. The granite extends for 2 kilometres from the north entrance. It is the same granite which enters into the structure of the Finsteraarhorn Massif. It is a coarsely crystalline, rather gneissic, granite. At a point about 1000 metres from the entrance and for about 500 metres further there is considerable differentiation; veins of various differentiation products traversing the rock, chiefly of white felspar, quartz, and a dense eurite. This region is indicated by Stapff upon the section. After the granite the rocks encountered (for a further distance of 2 kilometres) are sedimentary, and exist in the form of two parallel synclines. These rocks are believed to be of Trias-Jura age, and are recognized without in the Usern district. They include various altered sediments, some of which (as the Cipolin)

* Communicated by the Author.

Phil. Mag. S. 6. Vol. 23. No. 134. Feb. 1912.

P

are calcareous. It is not probable that these synclinal folds extend very deeply. The tunnel next enters the highly



metamorphosed rocks of the St. Gothard Massif. These extend for $7\frac{1}{2}$ kilometres, and include the most varied schists and intrusives; all showing the effects of intense dynamical

influences. Their age appears to be undetermined. The last section of the tunnel is through the sediments of the Tessinmulde, and extends a length of 3 kilometres. These sediments are also Mesozoic and are similar in many respects to the Usern rocks, of which they may be an extension.

The temperature gradients in the northern end of the tunnel were, as observed by Stapff*, of a very exceptional character. It is known that the thermal gradients in mountain regions are generally lower than is commonly observed in plains. The latter average about 30 metres to one degree, the former about 40 metres to one degree or even lower. Stapff, however, found the gradient at the northern end of the tunnel to be 20.9 metres per degree. The mean gradient in the central division of the tunnel was, on the other hand, only 46.6 metres. The rise in temperature at the northern end was by Stapff ascribed to the comparatively recent age of the granite: his view being that it was still parting with some of its original heat. That the source of heat is in the granite seems certain, for although the abnormal gradients extend into, and are indeed most marked where the tunnel traverses the Usern sediments, it is improbable that these sediments are directly influential. They probably are underlain, at no great distance downwards, by the granite, the heat from which escapes upwards through the intolded sediments.

The interest attached to the measurements of the radioactivity of the rocks arose from the coincidence observed between the temperature gradients and the radium content. Such a coincidence appeared clearly shown in the experiments. That the coincidence is of considerable suggestive interest will, I think, be admitted. If other coincidences of the same kind were discoverable there is no doubt that a strong case for ascribing some local gradients to radioactive effects would be established. Pending such discoveries I considered that the original observations in the radium content might with advantage be checked by further measurements. It was also desirable to measure the thorium content.

The thorium content of the original rock solutions was accordingly determined by a method possessing the requisite sensitiveness. The results were published in a paper in the *Phil. Mag.* for July 1909. The original radium measurements were also given in detail in this paper. It was found that the quantities of thorium in the granite at the north end of the tunnel were also in excess of those observed in the

* *Trans. North of England Mining and Mec. Engineers*, xxxiii. p. 25.

rocks of the central and south divisions. There was a similarity in the proportionate distribution of the two radioactive elements which may perhaps be regarded as an instance of the curious and as yet unexplained relation between the uranium and thorium content of many rocks.

The rock specimens originally dealt with were kindly given to me by the Trustees of the South Kensington Museum of Natural History, and consisted of chips removed from the series collected by Stapff during the construction of the tunnel. At a later date I ventured to apply for some further specimens. I have to thank the Trustees for again acceding to my request. The number of specimens applied for was 33; they were selected by Mr. Prior, whom I desire also to thank for the care with which the chips were selected and labelled. In this second selection I gave no guidance save the indication of the approximate position in the tunnel from which it was desirable the chips should come. These positions were selected so as to fill up the wider gaps left in the first selection. A few additional specimens in the form of a small collection purchased from MM. Grebel, Wendler et Cie, enabled me to add yet three more determinations among the granitic rocks at the north end. The purchased specimens were part of a Stapff collection and undoubtedly authentic. The total number of additional rocks obtained was 36. The original specimens numbered 51.

The examination of the additional specimens I postponed pending the development of a new method of determining the radioactivity of rocks, which would save much of the exacting labour attending the method by solution *. During the month of August last I accordingly examined the 36 rock samples in the electric tube-furnace.

The rock specimen to the amount of about 7 grams was reduced in the agate mortar to a degree of fineness sufficient to pass it through a sieve of 60 mesh to the inch, but no finer, as far as finer subdivision could be avoided. The powder after weighing was mixed with 28 grams of the mixed carbonates of sodium and potassium. The mixture was placed in a platinum boat and introduced into the furnace, which in some cases was raised somewhat in temperature before the introduction of the charge, in order that the volume of gas expelled into the gas-collector during the heating should not be too great for the electroscope. The temperature was raised for the last ten minutes to about 1100° C., the total duration of heating being about an hour.

* Phil. Mag. July 1911.

The expelled gases were passed through soda-lime and the unabsorbed gas received in a rubber bag, from which they were finally drawn into the exhausted electroscope: on the way passing again through the soda-lime tube. This is advisable, seeing that much of the emanation is probably retained in the tube into which it is borne along with the CO_2 expelled during the decomposition of the rock. A wash-out of the furnace-tube is finally effected by completing the filling of the electroscope through the entire system of furnace-tube and soda-lime tube. The chemicals used in this process were separately tested for radium emanation in the manner described, *loc. cit.* p. 147.

The electroscopes used were made of glass "bolt-heads," having a voluminar capacity of 500 c.c. The sulphur insulation was carefully shielded, by black paper tubes, from the light; past experience having showed that otherwise error might be occasioned. After a preliminary exhaustion and filling with air from the laboratory the rating of the movement of the gold leaf was carried on for about one hour before the admission of the gas, or for such a time as was necessary for the normal low reading of about 7 scale divisions per hour to be attained. If a higher reading—say, 8 to 12 scale divisions—persisted with no sign of diminution, this higher reading was subsequently deducted from the final readings. The filling from the furnace was effected through a capillary tube, which regulated the rate of inflow so that 8 minutes were required for the complete filling of the electroscope. The drying material used was phosphorus pentoxide, and a plug of tightly compressed cotton-wool was interposed between the drying-tube and the electroscope.

The determination of the constant, or calibration of the electroscopes, was effected as described, *loc. cit.* pp. 142, 146. There was some uncertainty about the constant of one of the electroscopes. Readings were obtained ranging from 0.6×10^{-12} to 0.8×10^{-12} . I am inclined to the view that the last value is the best supported; however, as comparative observations, which I effected by admitting to each electroscope the same volume of ground gas (drawn from a depth of 1 metre in the College Park), showed but little difference in the effects produced on the two instruments, and as the one exhibited very steadily 0.6×10^{-12} as the calibration value of a gain of 1 scale division per hour, I have thought it best to give the determinations made by the second instrument in terms both of the high and the low constant. The more important determinations applying to the Finsteraar granite

were, with two exceptions, made by the less variable instrument.

It is known that when radium emanation is admitted to an electroscope there is at first a rapid increase of the ionization due to the initial formation of the active deposit of short period. A marked slowing arises after about 10 minutes, and a temporary maximum is reached which persists till about the twentieth minute*. I have found that the rate of collapse of the leaf as observed during the period of temporary maximum is ultimately increased about 33 per cent. at the expiration of 3 hours. This observation applies both to the calibration tests and to the rock measurements. The labour of making the observations may be lessened by either calibrating the instrument for the effect in 15 or 20 minutes, and correspondingly reading the leak obtaining in 15 minutes, when rock experiments are being made. Or, again, we may use the calibration reading observed in three hours provided the reading obtained for the rock in 15–20 minutes is increased 33 per cent. It is true that the 33 per cent. is occasionally not fully attained and occasionally it is exceeded. Soddy has pointed out one source to which variations may be referred†. In a long series of measurements it is very improbable that any serious error can arise by the adoption of this method of reading the electroscope, and the gain in doing so is considerable, not only in the saving of time but in the better preservation of the electroscope. In the recent experiments herein recorded this method has been used for the greater number of the low results. In the higher and therefore more important and questionable readings the instrument was in every case but one allowed to stand for the full three hours, and in some cases for an additional hour.

The melts derived from the previous experiments were preserved in stoppered tubes and subsequently leached in water, filtered, and the residue acidified with thorium-free hydrochloric acid. The resulting solutions were examined by Mr. A. L. Fletcher for thorium, using the method described in the 'Philosophical Magazine,' May 1909, p. 760. I have to thank Mr. Fletcher for carrying out this work. The acid solutions alone were examined; as it has been repeatedly found that there is no appreciable amount of thorium removed in the first filtrate.

* Soddy, Phil. Mag. Aug. 1907, p. 280.

† Soddy, Phil. Mag. Dec. 1909, p. 848.

No. (Stapff).	Dist. from N. Entrance, Metres.	DESCRIPTION.	Radium gr. $\times 10^{12}$	Thorium gr. $\times 10^5$.
<i>Finsteraarhorn Massif.</i>				
1	0	Gneissic granite	5.2	1.8
6	304	Gneissic mica-schist, talcose	4.8	1.7
7*	408	Gneissic granite	3.4	2.2
8	540	" "	3.8	1.4
11*	700	" "	9.0	4.3
14	885	" "	5.5	2.7
16	957	" "	5.7	0.9
16*	957	" "	4.5	1.3
17*	1032	" " very quartzose ("gangartig") ..	3.6 (2.7)	2.3
19a	1099.5	Grey gneiss	6.1	3.2
20*	1121	Eurite ("gangartig")	1.7 (1.4)	0.6
23	1279.5	Gneissic granite	8.3	1.5
24*	1348.2	Aplite (white felspar)	2.9	1.3
26	1520	Coarse gneissic granite	7.9	2.0
26*	1520	" " "	7.3	2.6
27	1600	" " "	9.9	0.9
28	1700	" " "	8.1	2.7
29*	1800	" " "	8.1	3.3
30	1900	" " "	14.1	1.5
30*	1900	" " "	6.3	2.5
<i>Usenmulde.</i>				
33a	2116.8	Usen gneiss	3.2	1.4
36b	2278.9	Quartz-schist	5.4	1.1
38*	2383	Dark green schistose gneiss	3.7 (2.8)	1.9
42	2582	Black lustrous slate	6.8	0.2
44	2605.1	Grey cipolin	2.4	0.4
45*	2628.3	" "	0.7	0.9
47	2660.6	Quartzitic cipolin (zircon-bearing)	14.3	0.4
55	2765.8	Black lustrous slate	4.2	1.0
58*	2841.4	Greenish-grey schistose rock; "altered Usen gneiss"	1.3 (0.9)	2.0
61	2930	Usen gneiss	2.1	1.3
64*	3230	Bronze-coloured mica-schist ..	2.1	1.0
68*	3280	White sercite-schist with pyrites	2.7 (2.0)	1.7
71	3443.6	Sercite-schist	4.2	1.7
75	3756.2	Black lustrous schist	5.9	2.4
78*	3879.4	Grey, glistening schist; "Usen gneiss"	5.5	3.3
85	4038.8	Quartz-mica-schist	3.8	<0.3
91*	4257.4	Lustrous brown schist	2.2 (1.6)	1.0
90	4290	Usen mica-gneiss	1.7	0.5
<i>St. Gothard Massif.</i>				
92	4525.8	Querchen mica-gneiss	3.2	0.9
94a*	4704	Silvery mica-gneiss	3.7	1.1
95	4832.7	Hornblende rock	3.0	0.2
99	5250	Schistose serpentine	3.1	2.1
101a*	5310	Talcose schist	0.7 (0.5)	0.6
104*	5385	Brown mica-gneiss	5.0	1.5
107a	5734.2	Quartzose mica-gneiss	2.6	1.5
112	6075.4	" " "	2.6	0.5

No. (Stapff).	Dist. from N. Entrance, Metres.	DESCRIPTION.	Radium gr. $\times 10^{12}$	Thorium gr. $\times 10^5$.
<i>St. Gothard Massif (continued).</i>				
115*	6171.1	Brown glistening schist	0.8 (0.6)	1.8
114	6204.4	Quartz-felspar mica-gneiss	5.7	1.3
119	6426.9	Hornblende gneiss	8.4	0.8
116	6662.4	Gneiss	3.6	2.7
120*	6777.5	Gneissic granite	3.0 (2.3)	1.4
122*	6699.5	Brown mica-gneiss	3.5	1.4
124	6959.9	Gneiss	3.5	1.1
129b	7266.6	Fine-grained gneiss	4.6	0.7
133a*	7480-7530	Brown mica-gneiss	2.6	1.3
135	7695.3	Fine mica-gneiss	3.2	1.3
174	6741.1 from S. entrance	Quartz-felspar mica-gneiss	2.1	1.3
167	6081.2	Mica-gneiss	1.3	0.9
166	5994.3	"	1.8	2.3
162	5507.2	Mica-schist	2.5	0.1
160*	5372.8	Grey gneiss	3.1 (2.3)	0.4
158	5267.3	Mica-schist	2.2	1.5
154	5002.4	Hornblende mica-gneiss	4.8	1.7
148b*	4739.2	Mica-quartz-gneiss	2.3	1.1
145	4501.9	Sella gneiss	2.6	1.3
144*	4127.1	"	2.7 (2.0)	1.3
142	4078.2	"	2.7	0.7
137*	3738.6	Brown mica-gneiss	3.4	0.4
132	3353.5	Quartz-gneiss (zircons ?)	8.9	<0.3
130	3272.4	Mica-gneiss	9.2	1.5
<i>Tessinmulde.</i>				
121d	3049.2	Hornblende schist	2.7	<0.3
118*	2922.2	Coarse black mica-gneiss	1.2 (0.8)	0.0
117b*	2919.8	Fine quartz-schist with pyrites	1.6 (1.2)	0.3
111a	2792.8	Calcareous mica-schist	2.7	0.5
109	2682.9	Hornblende "	1.9	0.6
102b*	2545.6	Fine biotite-gneiss	2.2 (1.7)	0.6
95	2008.1	Amphibole-garnet mica-schist	4.3	1.0
92*	1871	Grey ore-bearing gneiss	1.6	0.4
86*	1756	Gneiss with garnets and pyrites	1.9 (1.4)	0.4
79	1528.3	Quartz-schist	6.5	<0.3
70	1014.5	Amphibole-mica-schist	2.1	0.5
63f*	868.3	Garnet-biotite-schist	2.5 (1.9)	0.6
61	632.2	Quartz-mica-schist	2.7	0.5
52*	304.5	Silvery gneiss	5.1 (3.8)	0.9
25*	92.8	Brown mica-schist	0.6 (0.4)	0.6
15	80.0	Dolomite	4.1	0.4
7*	60.5	Dolomitic tuff	1.2	0.2

In order to compare the new results with the old the earlier ones are reprinted in the table given above. The recent ones are interpolated in their proper order, and their distinguishing numbers marked with an asterisk. As regards

averages, it will be found that in the Finsteraar or northern section of the tunnel there is but little difference between the earlier and later radium measurements. The average of the former is 7.2×10^{-12} , of the latter 6.0×10^{-12} . In computing the latter, two experiments, Nos. 20 and 24, on vein substances are omitted. They are probably without bearing on the radioactivity of the granite generally, as they are, according to Stapff, "gangartig," consisting in the one case of a eurite or highly siliceous differentiation product, in the other of a white felspar from a "grobSPATHiger eurite." Both are shown in Stapff's marvellously detailed drawings as narrow white veins traversing the body of the granite. The one high result (14.1×10^{-12}) of the earlier results is largely influential in raising them above the later ones.

In the other sections of the tunnel the new experiments are distinctly lower than the older. Here, again, a very few exceptional rocks appear largely responsible. Two of these were zircon-bearing (as Stapff points out), *i. e.* No. 47 north end, which is a cipolin, and No. 132 south end. It will be noticed that the newer results in most cases conform in radium-richness to the neighbouring specimens. While I do not think the lower means point necessarily to errors of excess in the earlier results, it is certain that the method by fusion is safer than the method by solution; and, indeed, the process of extracting the emanation is almost of mechanical simplicity. It is not easy to go wrong in this part of the operation either by errors due to contamination or failure to liberate the emanation. The errors arising from light (or other causes) affecting the insulation of the electroscope are fully guarded against. I think, therefore, that the newer results are more reliable than the old, although I know of no source of error affecting the latter.

The following table gives the means for the several sections of the tunnel. The recent means are printed in italics:—

	Ra per gram $\times 10^{12}$.	Th per gram $\times 10^5$.
Granite and gneiss of the } Finsteraarhorn Massif }	7.2 <i>6.0</i>	1.85 <i>2.64</i>
Altered sediments of the } Usernmulde }	4.9 <i>2.6</i>	0.97 <i>1.70</i>
Schists, &c. of the St. } Gothard Massif }	3.9 <i>2.8</i>	1.18 <i>1.10</i>
Altered sediments of the } Tessinmulde }	3.4 <i>2.0</i>	0.51 <i>0.44</i>

Taking the means of both series of experiments we find the Finsteraar granite has a mean radium content of 6.7×10^{-12} and the Gothard Massif 3.5×10^{-12} for the radium, and 2.15×10^{-5} and 1.16×10^{-5} for the thorium. There is, therefore, about double as much of the radioactive substances in the granite as in the schists of the St. Gothard Massif. And this disparity is even greater in the new series of experiments, both in the case of radium and thorium.

It is interesting to compare the approximate heat equivalents of the radioactive bodies in the two important sections of the tunnel. Assuming that 1 gram of radium in equilibrium with all of its series involves 201.6 gram-degrees per hour, and that the same amount of thorium, also in equilibrium, involves 2.38×10^{-5} gram-degree per hour, we find the general means give for the radium 1351×10^{-12} calorie in the Finsteraar granite, and for the thorium 512×10^{-12} cal. The more recent experiments afford 1210×10^{-12} cal. for the radium. The total radioactive heat in this section of the tunnel is, therefore, 1863×10^{-12} cal. per hour, or 1722×10^{-12} cal., according as we take the general mean or the recent values of the radium content. These results are practically the same. In the St. Gothard or central section the general mean of the radium experiment gives 833×10^{-12} cal., and the mean of the recent radium experiment gives 666×10^{-12} cal. The heat due to thorium is 276×10^{-12} cal. The total heat is, therefore, 1109×10^{-12} or 942×10^{-12} calorie. These figures, where derived from the general mean, are based on a total of 87 rock samples taken at an average distance apart of 168 metres. The earlier series of rocks was selected so as to be representative of the more abundant rock species; the latter series was taken at random.

Stapff's gradient measurements give (as quoted above) 20.9 metres as the maximum in the granite and 46.6 in the St. Gothard schists. Assuming the conductivities the same, there is about double the amount of heat escaping from the granite than from the schists. There is probably not much difference in the conductivities. This point has been investigated in the case of the Simplon rocks*. In the Simplon the conductivity of the granite across stratification was found to be 0.0054 and along stratification 0.0069. The gneiss and schists across cleavage gave 0.0063 and along cleavage 0.0084. Stapff's explanation of the thermal state of the granite does not commend itself. The solidification of the granite must date back to Miocene times or

* See Mr. Fox's paper: Minutes, Proc. Inst. Civil Engineers, clxviii. p. 53.

earlier—certainly several millions of years ago. Prestwich gave a somewhat different turn to Stapff's theory in ascribing the heat to dynamical movements in the granite; movements which might have been of somewhat later date. But this source of heat was almost certainly inadequate. It appears difficult to urge a better hypothesis than that of the radioactive origin of the heat in a granitic mass extending deeply beneath the tunnel.

Unfortunately no other similar instance can be cited. The temperature observations in the case of the Simplon tunnel suggest themselves. Prof. Lees has calculated that a small amount of radium in those rocks would produce little effect*. A complete estimate of the radioactivity of the Simplon rocks has yet to be made. In view of the recent work which has been done in my laboratory, I must conclude that the general means for the Simplon rocks, which I formerly arrived at, may suffer from the same unknown source of error which apparently affected some other contemporaneous experiments.

Dec. 15, 1911.

XVIII. *On the Properties of the Rays producing Aurora Borealis.* By L. VEGARD, *Universitetsstipendiat, University of Christiania* †.

Introductory.

1. WE are at the present time quite familiar with the idea that the sun is sending out electric rays of some sort, and that such a radiation is the primary cause of Aurora Borealis and most magnetic disturbances.

Professor Kr. Birkeland ‡ has worked on this hypothesis for about fifteen years, and through a great number of observations treated by Birkeland and his collaborators, as well as through a number of laboratory experiments, a new light has been thrown upon these phenomena, and the results obtained are most strongly in favour of the radiation theory.

The theoretical work of Professor C. Störmer § on the

* C. H. Lees, Roy. Soc. Proc. A. vol. lxxxiii. p. 344.

† Communicated by the Author. Read before the British Association, Portsmouth, September 1, 1911.

‡ Kr. Birkeland, *Archives des Sciences phys. et nat. Genève*, 1896; *Recherches sur les taches du Soleil*, &c., 1899; *Expédition Norvégienne de 1899-1900*, &c., 1901; *The Norwegian Aurora Polaris Expedition, 1902-1903*.

§ C. Störmer, *Christiania Videnskabselskabs Skr., Math.-Nat. Kl. No. 3* 1904; *Archives des Sciences phys. et nat. Genève* [4] vol. xxiv. 1907.

orbits of electric rays exposed to the field of an elementary magnet, when applied to the sun and the earth, has also shown that the main features of the aurora and magnetic disturbances are simple consequences of the radiation hypothesis.

In fact I think that, all arguments collected and weighed, it will hardly be possible to doubt that electric radiation from the sun is the main cause of the phenomena in question. They show, however, a great variety of forms and variations, and further investigations will be required before we are able to follow each phenomenon into details, and, above all, we have at present no definite knowledge as to the *physical nature* of those solar rays which are engaged in the production of magnetic disturbances and the various forms of aurora borealis.

The determination of the nature of these rays will be of great importance, not only for the study of these most interesting terrestrial phenomena, but knowing the types of radiations we may obtain valuable information regarding the constitution of the sun.

It is my intention in this paper to give a contribution to the solution of the question regarding the physical nature of the electric radiation from the sun, by trying to show that certain auroral forms, especially the draperies, both as regards position, occurrence, structure, and form, are explained in a simple way by assuming that they are caused by α -rays, or rays having essentially the same properties, while the assumption of a radiation of the β -ray type meets with great difficulties.

This α -ray hypothesis was first announced by the writer in a note to 'Nature'*, and some further consequences have been drawn in a couple of notes recently published in *Archiv f. mat. og nat. Videnskab*.†

Properties of α -Rays.

2. Before proceeding to treat the auroral problem, let us first recall to our memory some of the most characteristic properties of α -rays.

The α -rays hitherto studied consist of helium atoms each of which carries an electric charge $+2e$.

The α -rays sent out during a certain transformation process will start with a quite definite velocity. As shown by

* L. Vegard, 'Nature,' no. 2163, p. 212 (1911).

† L. Vegard, *Archiv f. mat. og nat. Videnskab*, No. 6 and No. 9 (1911).

Bragg and Kleeman*, α -rays from a thin layer of radium bromide in radioactive equilibrium with its disintegration products, consist of a mixture of homogeneous groups corresponding to the various steps of transformation which are accompanied by the expulsion of α -rays.

The way in which α -rays are absorbed by matter is very characteristic for this type of radiation, and is very different from the law of absorption of β -rays.

Suppose a bundle of α -particles strikes a homogeneous layer of matter. The α -particle for the greatest length of its path will penetrate the matter in nearly straight-lined orbits, and only a comparatively small scattering takes place.

During the passage the velocity gradually diminishes, and after having traversed a certain thickness of matter called the range the α -particle loses its power of ionizing and of producing photochemical effects, and stops.

Bragg and Kleeman† have determined the range for various groups of α -radiation, and from the knowledge of the initial velocity we can find the relation between range and velocity. H. Geiger‡ recently measured the velocity (v) of the α -particle at different points of its path through matter, and found the following simple relation

$$v^3 = k(r - x), \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where x is the thickness traversed and r is very nearly equal to the range, and k is independent of x and v . If the various α -rays merely differ with respect to velocity, the relation between initial velocity V and the range R in a certain substance would be

$$V^3 = kR. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Bragg and Kleeman measured the relative amount of ionization produced by a homogeneous pencil of α -rays per unit length at various points along its path, and found the ionization to increase as the velocity diminished, first slowly, then more rapidly, and it *assumed a very marked maximum close up to the point where the rays are stopped*. On the assumption that the ionization (i) per unit length of path is proportional to the loss of kinetic energy, Geiger finds from equation (1) that $i^3 = \frac{k}{r - x}$.

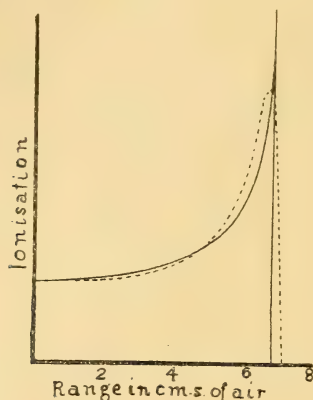
* Phil. Mag. [6] x. p. 318 (1905).

† Loc. cit.

‡ H. Geiger, Proc. Roy. Soc. A. lxxxiii. p. 505 (1910).

The theoretical and experimental curve is given in fig. 1, which is taken from Geiger's paper.

Fig. 1.



From observations of the absorption in various substances Bragg and Kleeman found that the masses of strata of equal absorption are proportional to the square root of the atomic weights.

Suppose we have a homogeneous layer of matter consisting of elements of atomic weight $A_1 A_2 \dots A_n$, then a stratum of total mass M per unit area has an absorbing power equivalent to a mass M' of air given by the expression

$$M' = 3.8 \left(\frac{I_1}{\sqrt{A_1}} + \frac{I_2}{\sqrt{A_2}} + \dots + \frac{I_n}{\sqrt{A_n}} \right) M, \quad (3)$$

where I_1 is the mass of the element A_1 for each unit of the total mass of the mixture.

H. Geiger* measured what he called the most probable scattering angle (λ) for the α -rays, and found

$$\lambda = K_0 \sqrt{AX},$$

where X is the air equivalent traversed, and A the atomic weight. This result, when interpreted, shows that on an average the α -particle will follow very nearly a straight line, the orbits will most of them only be slightly curved near the point where the particle stops, and consequently the track followed by a pencil of initially parallel rays will only very slightly broaden out from the track followed provided no scattering took place.

* H. Geiger, Proc. Roy. Soc. A. lxxxiii. p. 492 (1910).

Application to Aurora Borealis.

The Structure of Auroræ.

3. According to our present view, in the auroræ we are actually examining the luminosity produced when the electric radiation from the sun strikes the atmosphere, and from the form and structure of the luminosity we should be able to examine the way in which the solar radiation is absorbed by matter. In certain cases the form and structure is so characteristic and definite that we should be able to find out some definite properties with regard to the law of absorption of solar rays, and perhaps to identify them with some sort of known electric radiation.

One of the most conspicuous forms of aurora, showing very characteristic and definite properties, are no doubt the draperies.

Two drapery forms are represented in fig. 2; the one above

Fig. 2.



was observed at Godthaab; 1882, and the one below is from the classic work of P. Gaimard, ‘*Voyages en Scandinavie, en Laponie et au Feröe.*’

We notice the straight-lined structure, so characteristic for these forms. The simplest interpretation possible of the straight-lined streamers is to suppose that they mark the track followed by the solar rays as they penetrate down

the upper strata of the atmosphere. This interpretation is also in agreement with the fact that the streamers show a radiation point. We further notice that the straight-lined structure continues till the luminosity suddenly stops, forming a sharp edge of the drapery band.

In order to explain these straight-lined streamers, we must suppose that the solar radiation producing them shows a very small scattering, and we at once recognize one of the properties of α -rays. On the other hand, if the draperies are at all formed as the effect of radiation penetrating down the atmosphere, it is impossible to explain their structure by assuming a radiation of the β -ray type.

As shown by Crowther*, the β -rays are scattered at a rate which is enormously greater than the rate at which they are absorbed. Thus the β -radiation would be spread out in all directions as soon as it entered into the atmosphere, long before it was absorbed in any appreciable amount. Consequently, the luminosity produced would broaden out and become diffuse, and we should get no definite straight-lined streamers.

The small scattering of the solar rays, and the impossibility of explaining the draperies by β -rays, is also evident from the extremely small thickness of the drapery bands. Adam Poulsen, observing at Godthaab, has examined the bands from the bottom edge in the direction of the streamers, and he states that they appeared as if they had only linear dimensions and no observable thickness.

The suddenness with which the luminosity stops at the end of the streamers shows that the solar rays quite suddenly lose their power of producing luminosity. In other words, if we were to observe the solar rays by the luminosity produced, we should find that they possessed a well-defined range which in a striking way corresponds to the range of the α -particles as found from the ionization produced in a gas.

From the study of the discharge in rarified gases, we know that places showing great luminosity correspond to places where a great ionization takes place. The assumption is then a very legitimate one, that the luminosity produced by an α -particle along its path follows the same law as the ionization. If so, the maximum intensity of light at the edge of the band is simply explained if we suppose the ionization per unit length of path of the solar rays to follow a law essentially similar to that of α -rays (see fig. 1).

On examining and interpreting the structure of certain auroral forms, we have been able to show that the solar rays

* J. A. Crowther, Proc. Roy. Soc. A. lxxx. p. 186 (1908).

producing these forms, whatever their nature may be, have properties which are indeed most characteristic, and which are also found for α -rays, or, in another way of expression, *by giving to the solar rays properties which are physically known from α -rays we have succeeded in giving a simple explanation to a large class of auroral forms*, the explanation of which has so much puzzled earlier investigators in this field.

It would be premature, from these facts only, to identify the solar rays in question with α -rays; but in view of the fact that the drapery forms must be produced by some kind of electric radiation which cannot be of the β -ray type, I think we may reason from similarity in properties to similarity in nature, and suppose that these solar rays consist of atoms or molecules carrying an electric charge. It will be a matter of further investigation to determine more definitely the kind of carrier and charge necessary for the production of the aurora belonging to the class considered showing suddenly stopping straight-lined streamers.

The similarity between the electric rays from the sun and the α -rays makes it possible that at any rate certain forms of aurora may be produced by real α -rays from radioactive substances, and it will be of considerable interest to draw the consequences of such an assumption to see how far the α -ray hypothesis is in agreement with observed facts.

Absorption of α -Rays by the Earth's Atmosphere.

Height of Auroræ.

4. We shall suppose the barometric pressure (B) given as a function of the height (h) above the ground. If we do not take into account the variation of gravity with the height, the mass of unit area of stratum going from the upper limit of the atmosphere to the height (h) is $s.B$, where B is given in cm. mercury of specific weight s . If this mass (M) consist of a mixture of substances its equivalent mass of air (M') is found from equation (3). Provided the air equivalent is found corresponding to the height (h), equation (2) gives us the initial velocity of an α -particle which would penetrate down to this height.

In the numerical calculations we shall use values of B given by Wegener*. These numbers are based on various assumptions, *e. g.* they depend on the assumptions we make with regard to the gases present. Thus the distribution of pressure, especially in the strata above 100 km. say, cannot

* *Phys. Zeitschr.* xii. Nos. 5 and 6 (1911).

claim great accuracy, but we shall use Wegener's numbers as probably being of the right order of magnitude.

The relation between velocity and height is calculated for the following two cases:—

1. The matter traversed is air, velocity V_a .
2. " " hydrogen, velocity V_H .

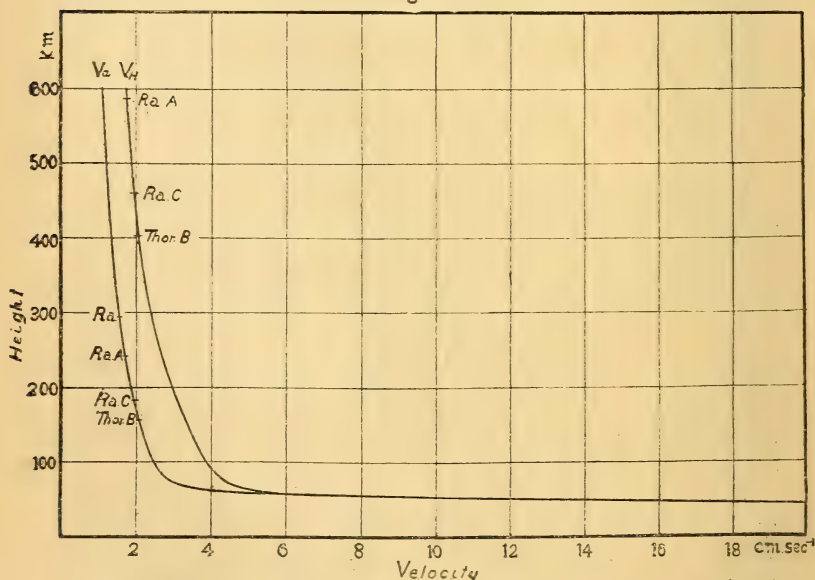
The results are given in the following table:—

TABLE I.

h .	B.	V_a .		V_H .	
km.	min.		cm./sec.		cm./sec.
500	0.00162	$0.62 V_0$	1.24×10^9	$0.97 V_0$	1.94×10^9
300	0.00329	0.79 "	1.58 "	1.24 "	2.48 "
200	0.00581	0.96 "	1.92 "	1.50 "	3.0 "
100	0.0128	1.24 "	2.48 "	1.94 "	3.9 "
60	0.106	1.51 "	5.02 "		
20	41.7	(18.4) "	(36.8) "		
0	760	(48.4) "	(96.8) "		

V_0 is the velocity of α -particles from Ra C, and is put equal to 2.0×10^9 cm. sec.⁻¹

Fig. 3.



The velocities corresponding to various values of h are illustrated in fig. 3. On each curve are marked a number of points corresponding to the range of the α -rays

given out by some known radioactive substances. We notice that down to a height of about 70 km. the value of (h) diminishes rapidly with increase of velocity, so that α -rays possessing a velocity about twice that of Ra C would get down to about 75 km.

Measurements of the height of auroræ have been made by a great many observers, and quite recently Störmer* has obtained measurements by means of a photographic method. Various observers give values which differ considerably; but it can be considered as quite certain that auroræ are most frequently found at a height interval, say, between 70 and 300 km. Störmer's observations gave a maximum of frequency at about 115 km. above the ground. Comparing calculated and observed values, we find *that the range of ordinary α -rays in matter is of the right order of magnitude to explain the height of the main bulk of auroræ boreales.*

The Diurnal Distribution of Auroræ and its Bearing on the Radiation Theory.

5. It has usually been held an indisputable fact that auroræ occur more frequently on the evening than on the morning side of the night. If there is such an asymmetry of distribution with respect to the plane through the sun and the magnetic axis, we might have a point of attack for the determination of the sign of the electric charge carried by the solar rays. Birkeland finds in the law of distribution stated an argument in favour of a negative radiation.

When the study of the structure of the auroræ led the writer to suppose a radiation of the α -ray type, it became a question of importance to make further investigations into the distribution of auroræ, and, provided it followed the rule stated, to see whether it would involve the necessity for a negative charge.

In the following pages I have attempted to give the diurnal distribution of certain auroral forms, and also to compare results with theory so far as such coordination is possible at the present stage of theoretical investigation.

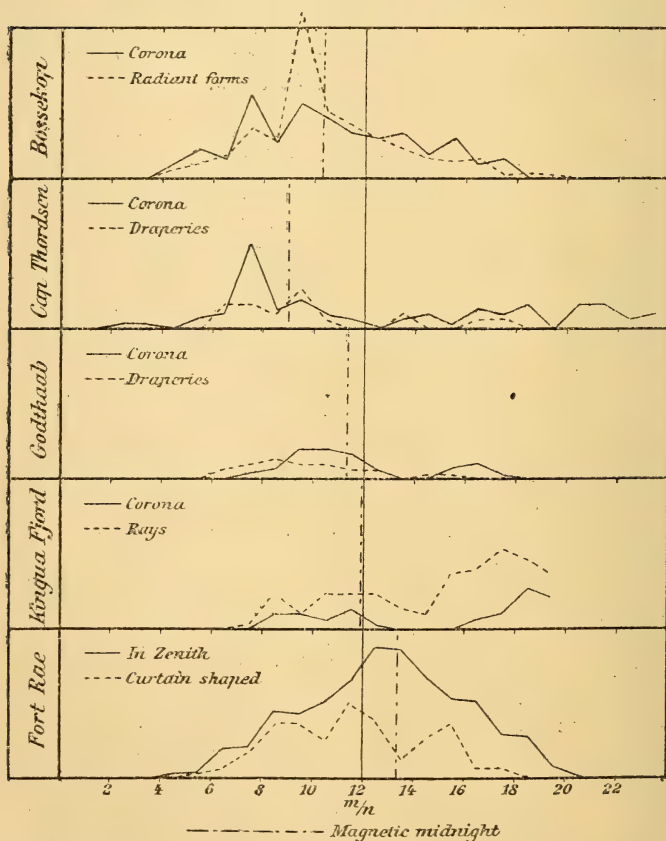
The determination of the diurnal distribution of aurora borealis meets with a great many difficulties. First of all, daylight will prevent auroræ from being observed during the day; secondly, the great variety of forms and intensities makes it very difficult to get a quantitative measure of auroræ which is free from any arbitrariness. Faults may also enter into the results from the sky being not equally well watched at different parts of the night.

* C. Störmer, C. R. 1911.

In dealing with the auroral problem I think we ought to be aware of the possibility that not all the luminous phenomena called northern lights are necessarily produced exactly in the same way and by the same agencies. Consequently, the diurnal variation may be different for different forms, and ought to be found for each type separately.

The types which mostly interest us in connexion with the α -ray theory are those which we might call *radiant forms*, containing all types of aurora showing definite streamers ending suddenly with a maximum of luminosity. To this

Fig. 4.
Winter 1882-83



group belong, *e. g.*, the draperies, the corona, rays and ray-bundles, a number of auroral bands, and probably some of the forms put down as arches may be merely distant aurora belonging to this group.

The apparent distribution of certain forms of aurora mostly belonging to this "radiant" group is given in Table II. and represented in fig. 4.

TABLE II.

Local hour.	BOSSEKOP.		CAP THORSEN.		GODTHAAB.		KINGVA FJORD.		FORT RAE.	
	Corona.	Radiant Forms.	Corona.	Draperies.	Corona.	Draperies.	Corona.	Rays and Draperies.	Curtain-shaped.	In Zenith.
1	0	0	0	0	0	0	0	0	0	0
2	0	0	0	0	0	0	0	0	0	0
3	0	0	1	0	0	0	0	0	0	0
4	0	1	0	0	0	0	0	0	0	0
5	3	9	2	0	0	0	0	0	0	2
6	6	16	3	0	0	0	0	0	1	2
7	4	22	3	5	0	2	0	0	2	12
8	17	49	17	3	1	3	0	1	5	13
9	7	37	4	8	2	4	3	3	11	27
10	15	163	6	2	6	3	3	7	11	26
11	12	67	3	0	6	3	2	7	8	31
12	9	53	2	0	5	2	4	7	15	39
m.n. 12										
13	8	39	0	0	2	2	1	7	12	53
14	9	31	2	3	0	0	0	4	4	52
15	5	21	3	0	0	1	0	3	8	40
16	8	18	1	0	2	1	0	11	11	32
17	3	20	4	2	3	0	2	12	2	31
18	4	5	3	2	1	1	3	16	2	18
19	0	7	5	0	0	0	8	14	0	17
20	0	4	1	0	0	0	6	11	0	5
21	0	0	5	0	0	0	0	0	0	0
22	0	0	2	0	0	0	0	0	0	0
23	0	0	3	0	0	0	0	0	0	0
.....	0	0	3	0	0	0	0	0	0	0

The results are deduced from observations recorded at

various polar stations during the polar year 1882-83. The numbers in the second to eleventh columns give for hour-intervals the total number of auroræ of the form considered which have been observed from the beginning of October 1882 to the end of March 1883. The form is given one mark each time it is observed, provided the time-interval between successive observations is greater than 0.2 hour. Thus the type counted is never given more than one mark in an interval of 0.2 hour, even when the same type has been recorded several times during that same interval.

In spite of the disturbing influence of daylight, the curves for the distribution during the night-time show the existence of one well-marked evening maximum, and also for the corona and drapery forms a well-marked minimum just after midnight. In most cases we also find a morning maximum, which, however, is not very well marked; and although its existence can hardly be doubted, the determination of its time of occurrence is rendered difficult, partly from the small frequency of auroræ at this part of the night, partly from the fact that it occurs so late in the morning that the daylight may have a disturbing influence on its position.

In Table III. is given the position of the various stations and the occurrence of the evening maxima.

TABLE III.

Station.	Latitude.	Longitude.	Form.	r .	Time of evening max.		α .	δ_m .
					Each form.	Mean.		
Bossekop	69° 57' N.	23° 15' E.	Corona	2.0	9.0 P.M.	} 9.25	14°.5	5°.5
			Radiant forms ...	2.9	9.5 "			
Cap Thorsden.	78° 28' N.	15° 42' E.	Corona	1.15	7.5 "	} 8.0	14°.5	4°.1
			Draperies	3.3	8.4 "			
Godthaab	64° 11' N.	51° 43' W.	Corona	2.5	10.3 "	} 9.8	22°	20°.9
			Draperies	3.4	9.3 "			
Kingua Fjord.	66° 36' N.	67° 15' W.	Corona	0.60	10.3 "	} 10.6	19°.1	24°.5
			Rays & Draperies.	0.32	10.9 "			
Fort Rae	62° 39' N.	115° 44' W.	Curtain-shaped ...	1.4	11.5 "	} 12.0	18°.9	22°.2
			In Zenith	0.61	12.5 A.M.			

The quantity r is the ratio between the number of auroræ observed before to those observed after midnight.

The curves show that auroræ are far from being equally distributed on both sides of midnight. This asymmetry

cannot be accounted for by any disturbing influence of daylight, because this light effect would be symmetrical with respect to midnight. The values of r show that at the three eastern stations, during the time of sufficient darkness, more auroræ of the forms considered appear on the evening side.

Kingua Fjord, however, occupies a most singular position in this respect; also here the auroræ show two maxima, but they occur with a decidedly greater frequency around the morning maximum than around that of the evening. This result is the more remarkable when it is compared with that of Godthaab. This station is situated very nearly on the same latitude as Kingua Fjord, and is not very far apart from it, and further, the observations at the two places cover the very same period.

Passing on to the most westerly station, Fort Rae, we find that the value of r increases again. For the curtain form it is greater than one, and for auroræ through the zenith somewhat less than one; but this fact does not show, as in the case of Kingua Fjord, that more auroræ are found near the morning maximum; it is rather a consequence of the fact that the evening maximum occurs much later at this station than at the more easterly ones.

The evening maximum is seen to occur at very different local hours. At Cap Thordsen it occurs as early as 8 o'clock, while at Fort Rae it occurs at 12. The occurrence of the maxima at the various stations will become more regular when regarded in relation to the magnetic axis instead of the axis of rotation of the earth. Let on a geocentric sphere O be the position of the station, S that of the sun at the moment of the evening maximum, and P and P' the points where the axis of rotation and the magnetic axis cut the sphere respectively.

The hour angle of the sun SPO is given by the local time of the occurrence of the maximum. The corresponding angle with reference to the magnetic axis is $SP'O$, and has been calculated for the various stations. The angle α given in Table III. is supplementary to $SP'O$ or $\angle SP'O = 180^\circ - \alpha$.

In Table III., $90^\circ + \delta_m$ is the angle between the north direction of the magnetic axis and the direction to the sun at the time of the evening maximum.

In spite of the great differences of the hour-angle OPS the angle $SP'O$ comes out nearly constant. This will also be evident from fig. 4 (p. 220), where a line is drawn giving the time when the station cuts the plane through the sun and the magnetic axis, or, as we might call it, the time of *magnetic midnight*.

The values of α show that for all stations the evening maximum for the winter 1882-83 occurred about 1.3 hours before magnetic midnight.

We saw that auroræ did not occur symmetrically with regard to a plane through the sun and the axis of rotation. Looking at the curves, we notice that there is also a marked asymmetry with respect to the magnetic midnight, or with respect to a plane through the sun and the magnetic axis.

Application of Mathematical Theory.

6. Störmer's † calculations, founded on the radiation hypothesis, should give us some means of determining from theory the diurnal distribution of auroræ. The part of his researches which mostly interests us is the determination of the orbits through the origin ‡, and we shall mention a few of the results which have reference to our problem.

According to Störmer we get the various types of orbits through the origin (the centre of the earth) by the variation of a single integration constant γ . In order that rays starting from the origin shall pass on towards infinity γ cannot be outside the interval (I)

$$-1 < \gamma < 0.$$

But values of γ inside this interval may or may not give orbits through the origin with infinite branches.

Numerical integration has shown that all values of γ in the interval (I₁)

$$-\gamma^* < \gamma < 0,$$

give orbits through the origin which pass on towards infinity, γ^* is found to be about 0.93. In the rest interval (I₂) $-1 < \gamma < \gamma^*$ there are an infinite number of orbits which only reach a certain distance and then go back to the origin; but also in this interval an infinitely large number of orbits are found which have infinite branches.

If the rays from the sun reach the earth they must follow some path which is very near to one of those coming from the origin, and if the quantity $c = \sqrt{\frac{M}{H_0 \rho_0}}$ § is less than the distance between the sun and the earth, the rays

† *Loc. cit.*

‡ See C. Störmer, *Archives des Sci. phys. et nat. Genève*, pp. 235-247 (1907).

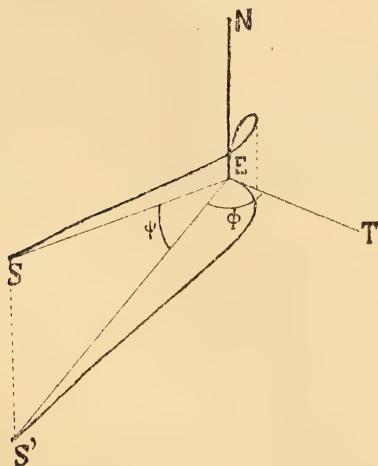
§ M is the magnetic moment of the earth, ρ_0 is the radius of curvature of the ray when moving in a uniform field of strength H_0 in a plane perpendicular to the magnetic force.

from the sun which are to reach the earth must follow near to orbits through the origin having infinite branches. The condition mentioned only requires $H_0\rho_0 \geq 0.38$, and the solar rays giving rise to the radiant forms here considered must undoubtedly fulfil this condition, on account of the fairly great penetrating power they possess; for it only means that the solar rays must be less deflectible than a cathode particle which has acquired its velocity from a potential fall of about 1/100 of a volt.

In order to get an idea of the diurnal distribution we may regard the distribution of precipitation of electric radiation, which at a certain moment would be produced by a rich supply of radiation from the sun

Suppose the rays to come from a point S whose distance from the point E corresponds to that between earth and sun. Let SE, fig. 5, form an angle ψ with the plane perpendicular

Fig. 5.



to the magnetic axis. Suppose the orbit to be projected on this plane, and let the tangent (ET) of the projected orbit at the origin form an angle Φ with the line S'E. As shown by Störmer, Φ and ψ are single-valued functions of γ ; but we have to remember that Φ and ψ only exist physically for intervals of γ which give orbits through the origin with infinite branches.

Numerical integration has shown that the two functions $\Phi = f_1(\gamma)$ and $\psi = f_2(\gamma)$ are continuous and real in the interval (I_1) ; in the interval (I_2) , however, if we only consider real values, the two functions $f_1(\gamma)$ and $f_2(\gamma)$ have a

great number of points of discontinuity corresponding to orbits which do not pass on towards infinity, and the curves $f_1(\gamma)$ and $f_2(\gamma)$ break up into a number of separate parts. These curves have not yet been exactly determined; but from Störmer's investigations we see this much, that in the interval (I_2) ψ will oscillate inside a fairly small interval, while the angle Φ , especially for orbits near those returning to the origin, may assume enormous values. In other words, the orbits of this interval may turn several times round the magnetic axis before they strike the earth.

As such a large variety of orbits corresponds to a very small interval of γ , very small variations in the initial conditions may cause great changes in the form and position of the auroræ. Consequently, we should expect that auroræ, as far as they are produced by rays following orbits of the interval (I_2), would on an average be spread over all hours of the day, and we should not expect auroræ formed in this way to produce very distinct maxima or minima. At the present stage of mathematical investigation we are not able either to prove the existence or to determine the position of such possible maxima corresponding to the interval (I_2). For the auroræ possibly belonging to the interval (I_1), however, we can estimate the position of the diurnal maxima.

A number of orbits of the interval (I_1) are given in fig. 6, which is a photograph of a curve model made by Störmer. The orbits are all supposed to come from points situated in the same plane through the magnetic axis, and at a distance from the origin equal to that between earth and sun. Curve A, fig. 7, shows the relation between Φ and ψ in this interval. When γ passes from 0 to -0.93 Φ increases from 0° to 306° .

The position of the spot of precipitation is determined from theory by the position of the sun relative to the magnetic axis, and will be given by the points of intersection between the curve (A), fig. 7, and the straight line (B) given by the equation $\psi = +\delta_m$, where $90^\circ - \delta_m$ is the angle between the direction to the sun and the north direction of the magnetic axis.

The distribution previously found is derived from observations during the winter. In that case δ_m is negative, and the line B will intersect the curve A in four points, corresponding to four diurnal maxima. The first and the last one occur in the day and escape our observations. The points m_1 and m_2 are about symmetrically situated with respect to magnetic midnight and correspond to night maxima.

Thus the observations are so far in agreement with theory

Fig. 6.

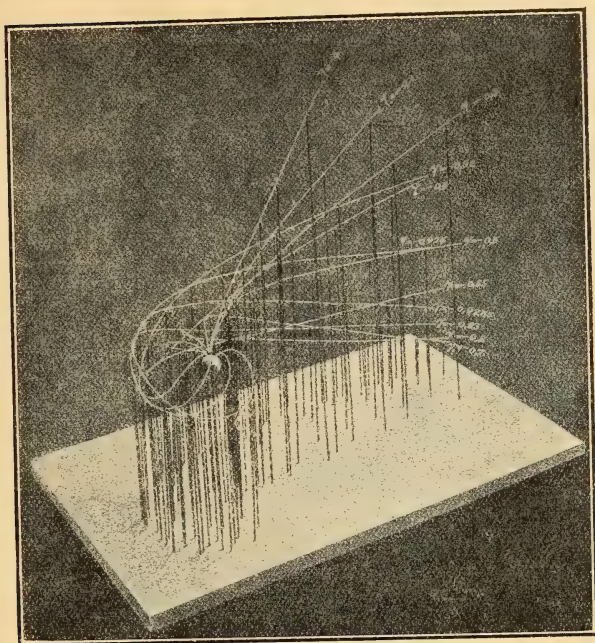
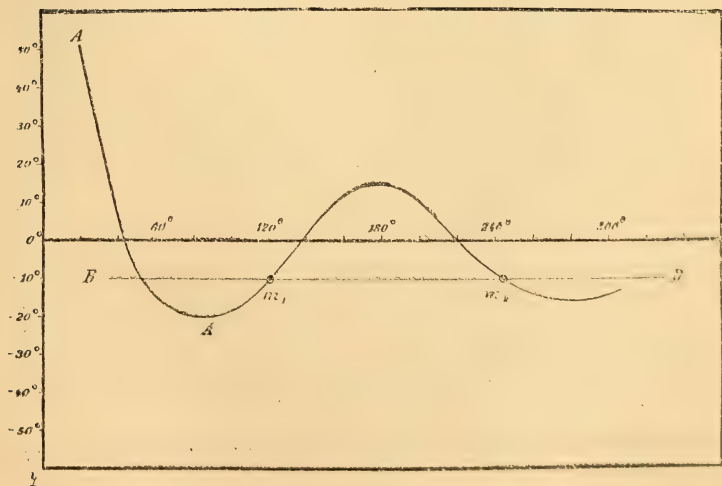


Fig. 7.



that the mere existence of two night maxima, one before and one after midnight, is a consequence of mathematical theory; but entering into details we should meet with many difficulties if we were to suppose that the predominant part of auroræ observed belonged to the interval (I_1).

Thus the two night maxima observed at the various stations are not symmetrical with respect to magnetic midnight, which should follow from theory provided the station was situated near the meridian passing through the magnetic axis (P'). Such a position has Kingua Fjord, but still the morning maximum occurs more than six hours after, while the evening maximum occurs only two hours before midnight.

Another difficulty arises from the fact that auroræ occur when δ_m has such large values that the line $\psi = \delta_m$ does not hit the curve A at all. Thus at Kingua Fjord the average value of δ_m at the time of the evening maximum is $24^\circ.5$, and at midwinter even much greater, the largest (negative) value of ψ in the interval (I_1) is no more than 20° .

Further, the diurnal maxima are not by any means so sharp as should be expected from theory, provided most auroræ were caused by the rays following orbits of the interval (I_1).

The broadening out of the maxima may have several causes. In the first place, auroræ are observed and may be counted even when they do not appear with their main bulk on the meridian of the place. Secondly, the curves are deduced from observations covering a period of several months, and during that time δ_m will undergo variations which will produce corresponding changes of Φ or the time of occurrence of the maxima. But these causes alone are not competent to explain the broadening of the maxima; for the same form may be observed near the zenith repeatedly for many hours during the very same evening; neither can it be due to differences of stiffness* of the solar rays, because, according to mathematical theory, when ψ is the same, the value of Φ is very little changed by considerable changes of stiffness.

The discrepancies, however, may to a certain extent be ascribed to the incompleteness of the mathematical investigations, because the path of the rays near the earth may be greatly different from that of an elementary magnet, and near the poles a small difference of path may considerably alter the hour of occurrence.

* "Stiff rays" means rays which are not easily deflected by electric or magnetic forces.

The simplest way of explaining the indistinctness of the maxima is to suppose a great part of the auroræ to correspond to the interval (I_2). The great variety of forms of the orbits will also best account for the great variety of forms of auroral bands, and their rapid and often irregular motions.

7. Finally, we shall consider the question as to whether the distribution of auroræ is consistent with the assumption of a positive radiation.

Let, in fig. 5, the north pole be turned upwards, then the orbits drawn correspond to negative rays. The positive rays will have quite a similar course, only that they turn round the magnetic axis in the opposite direction, or orbits of positive rays are the mirror image of the negative ones with respect to a plane through the sun and the magnetic axis.

Now if the rays are negative the aurora occurring before magnetic midnight should correspond to Φ less than 180° . In accordance with the suggestion made by Birkeland I suggested, in a note to 'Nature'*, that the greater frequency of auroræ on the evening side compared with that on the morning side should indicate a negative radiation. This supposition is based on the assumption, which indeed might seem quite a reasonable one, that the simplest orbits, those corresponding to the interval $0 < \Phi < 180^\circ$, should occur more frequently than orbits for which Φ is greater than 180° .

The mathematical theory, however, is not yet carried so far that the probability of the occurrence of various orbits has been found; but still the calculations made enable us to draw certain conclusions.

Looking at the curve A we notice that for values of Φ less than about 35° , ψ is greater than any of the values δ_m can have, or radiation from the sun cannot at all follow those very simplest orbits passing from the earth towards infinity, because the sun cannot take up the position required.

Moreover, the results for Kingua Fjord are an exception to the rule that more auroræ occur round the evening than round the morning maximum. But even in the cases where the rule of the greater evening frequency holds, a negative charge of the rays is by no means a necessary consequence.

Provided the interval I_2 is excluded, Φ is found to be less than 360° and the value of Φ corresponding to the evening maximum is $180^\circ + \alpha$, where α at the various stations has the fairly small values given in Table III., and the sign + corresponds to a positive, the sign - to a negative radiation.

The theory gave two night maxima about *symmetrically* situated with respect to magnetic midnight. Thus both

* *Loc. cit.*

$\Phi = 180^\circ + \alpha$ and $180^\circ - \alpha$ may equally well correspond to a theoretical maximum; and thus, if we consider the auroræ regardless of their peculiar forms, the theory gives no reason for supposing orbits corresponding to $\Phi = 180^\circ - \alpha$ more probable than orbits corresponding to $\Phi = 180^\circ + \alpha$.

So far the theory of the diurnal distribution leaves the question with regard to the sign of the charge undecided.

If, however, we take into account the theoretical conditions for the formation of various forms, e. g. the draperies, we may get a step further.

Störmer, from his mathematical investigations, has succeeded in giving a fairly simple explanation of the formation of the thin and long drapery bands. Regarding details I must refer to his papers*. It may here be sufficient to notice that it is essential for his explanation that Φ has a great value, at least greater than 180° . If the rays correspond to the interval (I_1) Φ must be in the interval $180^\circ < \Phi < 360^\circ$, and if they follow some infinite orbit of the interval (I_2), Φ might be even greater.

Thus, according to Störmer, the draperies, so far from being produced by the simplest orbits, are rather caused by rays following the more complicated ones, and *thus the reason for supposing that a negative radiation produces the draperies loses its foundation.*

In all cases investigated most drapery forms are found near the evening maximum: if so a positive radiation is the more likely; for, in the case of a positive radiation, the production of an evening maximum of drapery forms would only require $\Phi > 180^\circ$, while in the case of a negative radiation it would require $\Phi > 360^\circ$.

Explanation of Equidistant Bands.

8. The explanation of a thin drapery band given by Störmer requires a radiation which is strictly homogeneous.

But, whatever the explanation may be with regard to details if we at all stick to the hypothesis that auroræ are formed by electric radiation from the sun, a homogeneous radiation will be necessary to account for the very sharp boundaries of extremely thin drapery bands; for a heterogeneous radiation composed of rays whose stiffness varies fairly continuously between wide limits will produce a broad and diffuse band. This follows from the law of motion of electric rays in the earth's magnetic field, because a variation of stiffness will correspond to a motion of the point where the ray strikes the

* *Arch. des Sciences*, &c. p. 336 (1907).

atmosphere taking place nearly perpendicular to the magnetic parallel along which the bands are usually directed. And if our interpretation of the structure is right, the sharp bottom edge of the drapery bands will require rays with the same penetrating power.

Now, on the other hand, we know that α -rays given out from a radioactive compound during one single radioactive transformation are in fact homogeneous, and consequently *α -rays from some radioactive compound are just the proper agency for the explanation of drapery bands.*

Another most characteristic and peculiar property of auroræ is the existence of equidistant bands (see fig. 2), and in order to explain their formation we shall merely have to suppose that each band corresponds to its own homogeneous radiation. In other words, *the radiation must be composed of a mixture of distinctly different homogeneous groups of rays*, and at the same time we must suppose that *these groups are all of them given out simultaneously from the same source on the sun and subject to the same initial conditions.*

These two conditions being present the mutual relation found between the bands will be easily understood. For the sake of simplicity we suppose only two groups to be present in the source.

Two rays, one of each group, leaving the source simultaneously along the same line, we shall call corresponding rays, and the points where they strike the atmosphere corresponding points.

Suppose now the conditions to be such that one of the groups gives rise to a band. If the difference of deflectibility is fairly small the second group will also strike the atmosphere. Now the difference of path of corresponding rays is entirely due to a different deflexion in the magnetic fields traversed, or to the difference of stiffness of the two groups which is a definite quantity, consequently the distance between corresponding points will vary continuously along the first band; and according to Störmer's calculations, when the band is extended nearly along the magnetic parallel, the corresponding points should keep their distance nearly unaltered all along the band, and each pair of corresponding points should be situated nearly on the same magnetic meridian. Thus the entire collection of corresponding points will form a band running nearly parallel to the first one.

Suppose the system to undergo a gradual change, which, *e. g.* may be due to a motion of the magnetic equator relative to the sun. Such a change may produce a motion of the bands; but if the two groups of rays are still sent out from

the same source, the one band must at any moment be equidistant with the other, it would appear as if the bands in a mysterious way were attached to each other. Indeed, such a motion is most characteristic, and often observed for a system of parallel auroral bands.

If we did not know the radioactive processes, it would indeed seem a rather artificial explanation, which was built on the assumption of a mixture of homogeneous rays given out from the same source; for any kind of electric discharge producing such conditions is almost inconceivable. On the other hand, when we assume a kind of α -radiation to produce the bands such conditions are not only conceivable, but may rather be considered a necessary consequence, because a number of radioactive compounds intimately mixed, each producing its own homogeneous α -radiation, will be formed by atomic disintegration of some parent substance.

In this connexion it may be well to remember that any homogeneous radiation would have to start from the sun in such a way that the rays were able to pass into space without traversing any appreciable layers of matter, and if radioactive substances formed the source, they would have to exist in very thin layers. A radioactive emanation ejected from the sun and disintegrating would fulfil all necessary conditions.

From our point of view the drapery bands should give a kind of *magnetic spectrum* of the homogeneous groups of α -rays present in the source, and as the α -rays are characteristic of the substances emitting them, a possibility opens out of studying or identifying the family of radioactive substances present in the sun by observing the relative distances between the various bands.

If we adopt the simplified system of an elementary magnet we may, from a formula given by Störmer, calculate the position of the bands caused by α -rays from a certain family of radioactive substances.

Let ω denote the angle between the magnetic axis and a line from the earth's centre to the band, and let D be the distance from the centre of the earth to the bottom edge of the band, then

$$\sin \omega = \sqrt{2\gamma_1 \frac{D}{c}}, \text{ where } c = \sqrt{\frac{M}{H_0 \rho_0}}.$$

For the draperies to be formed γ_1 must be between 0.9 and 1. A change of ω corresponding to a change of deflectibility is found from the relation

$$\Delta \omega = -\frac{1}{2} \tan \omega \frac{\Delta c}{c}.$$

For α -rays from radium emanation we find $\omega = 16^{\circ}5$. This result is a most important one when taken in connexion with the position of the auroral zone. According to the chart given by Fritz, the auroral zone for equal frequency on the northern and southern sky is situated at an angular distance from the magnetic axis of about 17° or 18° , consequently α -rays of the ordinary kind have just the proper stiffness to give the right position of the auroral zone.

The relative position of the bands corresponding to α -rays from the radium family is given in the following table:—

TABLE IV.

Substance.	Distance from Ra band.	Distance between successive bands.	Apparent angle between succes. bands.
Ra	0 km.		
Pol.	24 "	24 km.	$11^{\circ}5$
Ra Em. ...	39 "	15 "	$7^{\circ}2$
Ra A	64 "	25 "	$11^{\circ}9$
Ra C	133 "	69 "	33°

The bands are supposed to be seen near the zenith at a height of 120 km.

The material at my disposal gives no means of any exact comparison with observations. Such comparison, however, may be possible by the development of the photographic method. But this much can already be said, that the values found are of the right order, or, differences of stiffness as those of α -rays from ordinary radioactive substances are competent to explain the distances between successive bands actually observed.

The Light of Aurora.

The various lines in the auroral spectrum have not yet been interpreted with any certainty by means of spectra physically known. The greater number of lines have probably rightly been identified with lines of the spectrum of air and some of the rare gases; but the origin of the most conspicuous line with the wave-length $\lambda = 5570$ is still unknown.

As early as 1874 Ångström* came to the conclusion

* Ångström, Pogg. Ann. Jubelbd. p. 424 (1874).

that the line 5570 was due to fluorescent or phosphorescent light. Later on, A. Schuster* called attention to the fact that this auroral line very nearly coincides with one of the krypton lines ($\lambda = 5570.4$). According to Kayser, however, this coincidence does not prove identity of the two lines; for the auroral spectrum does not give the other krypton lines with the intensity to be expected from the ordinary krypton spectra.

The difficulty in interpreting the auroral spectrum indicates that the spectrum depends essentially on the peculiar way in which it is produced.

According to the view put forward in this paper, the light is produced by an electric radiation of the α -ray type penetrating down the upper strata of the atmosphere. At present we do not know very much with regard to the nature of the light produced in this way.

The spontaneous luminosity given out from RaBr_2 has been examined by Sir William and Lady Huggins†. They found the part of the spectrum examined to be essentially similar to the *negative* band spectrum of nitrogen, and besides they found a band (about $\lambda = 5165$) the origin of which they were unable to explain. From the fatigue effect produced by hydrogen they concluded that the β -rays did not greatly contribute to the luminosity, which they supposed to be given out from the region inside the solid substance.

B. Walter‡ was the first to show that light was also given out from the air surrounding the radioactive substance. He experimented on polonium and found a spectrum similar to that of radium bromide; but in the case of polonium it more resembled the *positive* band spectrum of nitrogen.

R. Pohl§, F. Himstedt and G. Meyer||, showed that, also in the case of radium bromide, the surrounding air gave out a faint luminosity which could be detected photographically. R. Pohl states that luminosity in the air can be observed several centimetres from the substance.

As polonium only gives out α -rays and the very absorbable δ -rays which do not ionize, the luminosity given out from the air several centimetres from the substance must be produced by α -rays.

When we are going to make comparison with the auroral

* A. Schuster, 'Nature,' No. 58, p. 151 (1898).

† Sir William and Lady Huggins, Proc. Roy. Soc. lxxii, pp. 196 and 409 (1903); lxxvi, p. 488 (1905).

‡ B. Walter, *Ann. d. Physik*, xvii, p. 367 (1905); xx, p. 327 (1906).

§ R. Pohl, *Verh. d. D. Phys. Ges.* vii, p. 458 (1906).

|| F. Himstedt and G. Meyer, *Ber. d. naturf. Ges. zu Freiburg in Br.* xvi, p. 13 (1905).

spectrum, however, we must remember that the auroræ are produced under circumstances very different from those present in the previous experiments. Thus the solar rays have a much greater density and penetrate through rarified gases and perhaps also fine dust particles, and these differences might account for the greater number of lines observed in the auroral spectrum and the appearance of the auroral line $\lambda=5570$.

The spectrum of the phosphorescent light produced by α -rays falling on certain substances has been examined by E. Marsden*. Zinc sulphide gave a single band extending from $\lambda=5920$ to $\lambda=4250$, and willemite a band between $\lambda=5800$ and $\lambda=4870$. The auroral line falls in the middle of these bands.

The spectral analysis at its present state may indeed furnish us with certain suggestive points; but it does not give an *experimentum crucis* for the determination of the nature of those rays which produce aurora borealis. We shall have to wait for further experiments; but already the previous experiments have shown that α -rays (compared with the other radium rays) are very effective in producing luminosity in the air through which they pass, a property which is very essential if rays of this type are to explain the brilliancy of auroræ.

Rays consisting of atoms or molecules might not only make the matter through which they pass luminous, but by their impact they might themselves give out light. If so, we should have a means of investigating the nature of the carrier by observing the Doppler effect in the auroral spectrum of those lines which are produced by the radiation itself.

The spectrum analysis of the light produced by α -rays, however, gave no trace of helium lines. Thus in this case the light given out from the carrier is either wanting or very feeble as compared with that produced in the surrounding air.

The difficulty in detecting a possible spectrum from the carrier is made even greater through the Doppler effect, which for the very large velocities would amount to about one-tenth of the total wave-length. The light from the auroræ entering the spectroscope will usually correspond to directions forming the most different angles with the direction of the radiation; consequently the light corresponding to a certain line from the carrier would be spread out to a

* E. Marsden, Proc. Roy. Soc. A. lxxxiii. p. 548 (1910).

fairly broad band, which in the green spectrum may cover as much as 500 Å.

The definite sharp lines observed in the auroral spectrum are therefore no doubt due to light produced in the atmosphere, and do not originate from the radiation itself.

Concluding Remarks.

From the study of the structure of the radiant forms of aurora, we found that the rays producing them had a number of characteristic properties in common with α -rays.

The investigation with regard to diurnal distribution showed that, so far as our present knowledge goes, the assumption of a positive charge is not only a legitimate one, but is even the most favourable for the explanation of the occurrence of drapery forms.

From the point of view of the radiation hypothesis the extremely thin drapery bands have to be produced by a strictly homogeneous radiation, and the parallel bands were explained in a simple way by assuming groups of homogeneous rays to emanate from the same source. This explanation gave a strong argument in favour of the view that the solar rays are not merely of the α -ray type, but are indeed α -rays of some sort given out from radioactive substances.

With regard to the position of auroræ, we found that the stiffness of ordinary α -rays gave the right distance from the magnetic axis, and their penetrating power was sufficient to account for the altitude of a great part of the auroræ observed.

Thus, as far as our investigations have been carried, the ordinary α -rays are found to possess the right charge, scattering, stiffness, and penetrating power, which are necessary to explain most characteristic properties of a great number of auroræ.

But still we ought to be aware of the possibility that not all auroral forms are necessarily produced in the same way and by the same radiation. It is quite possible that auroræ in certain cases may partly be secondary effects of precipitations of solar rays, and that certain diffuse forms may be produced by corpuscular rays. And even in the case of the radiant forms with straight-lined structure, it is still a matter for further investigation to determine in each case the atoms or molecules which form the carriers of the electric rays.

Provided relation (2) holds good for all possible velocities, we found that an ordinary α -particle, even with the velocity of light, could not reach within a distance of 27 km. from

the ground. On the other hand, many observers have found auroræ, especially rays and ray-bundles, to reach within a distance of one km. If so, the rays must possess an enormous penetrating power, and yet the straight-lined structure will make a radiation of the α -ray type necessary; but it is a type not yet known from laboratory experiments.

It is a remarkable fact that the rays and ray-bundles often shoot down in between other forms of aurera which do not reach so near to the earth. In view of our radiation hypothesis, this would mean that these very penetrating rays had about the same stiffness as ordinary α -rays, or

$$\frac{mv}{ne} = \frac{m_0v_0}{2e} \text{ (approximately),}$$

where m and v are respectively the mass and velocity of the solar rays and ne the charge of each particle; m_0 , v_0 , and $2e$ are the corresponding quantities for α -rays.

From what we know about the charge carried by the small ions and by the positive rays in vacuum-tubes, n ought to be a very small number. Then in order to explain the great penetrating power of the solar rays, we should have to suppose a carrier smaller than a helium atom, but moving with a velocity so much greater than that of α -rays that the above relation is fulfilled. The carrier might either be hydrogen or some gas lighter than hydrogen, and the possibility suggests itself that coronium may form the carrier of the most penetrating solar rays.

XIX. *Note on the Cosine Law of Radiation.* By LOUIS VESSOT KING, B.A. (Cantab.), Lecturer in Physics, McGill University*.

§ 1. IT is a well-established fact in the theory of light that the intensity in a parallel beam of homogeneous radiation travelling a distance x through an absorbing medium is diminished according to the exponential law

$$I = I_0 e^{-\kappa x}, \dots \dots \dots (1)$$

where I_0 is the intensity over unit cross-section measured at an arbitrary origin $x = 0$. κ is a constant for the medium, called the *coefficient of absorption*, and depends on the wavelength of the radiation.

If the radiation emanate from a point-source s , we consider

* Communicated by Prof. H. T. Barnes, F.R.S.

the diminution of intensity between the portions S and $S + dS$ of two spherical surfaces of radii r and $r + dr$ cut out by a small solid angle ω .

We then have

$$S dI = -I dS - IS\kappa dr.$$

The first term on the right-hand side expresses the diminution of intensity per unit cross-section due to the increase with r of S to $S + dS$, while the second term expresses the diminution of intensity by absorption in a distance dr .

Since $S = \omega r^2$, we have in a uniform medium (κ independent of r),

$$\frac{dI}{I} = -2 \frac{dr}{r} - \kappa dr,$$

giving

$$I = \frac{C}{r^2} e^{-\kappa r}$$

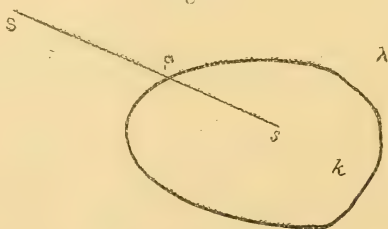
where C is a constant of integration.

As long as S remains in the same medium as the point-source s , we may write the above in the form

$$I = \frac{s}{r^2} e^{-\kappa r}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where s is the intensity across unit-area at unit-distance when there is no absorption ($\kappa = 0$), in which case (2) simply expresses the law of inverse squares.

Fig. 1.



Suppose s to be in a uniform medium whose coefficient of absorption is κ , while the intensity is measured in a medium of coefficient λ , the two media being separated by a surface cutting sS at a point P such that $sP = R$. Then provided we neglect effects of refraction and reflexion at the bounding surface, a condition which is justifiable in the application to be dealt with, we may consider the path of the rays forming the pencil of small solid angle ω to be unaltered in crossing

the boundary. Under these conditions the intensity at P in the medium κ is given by

$$I_{\kappa} = \frac{s}{r^2} e^{-\kappa r},$$

while the intensity in the medium λ is given by

$$I_{\lambda} = \frac{C}{r^2} e^{-\lambda r}.$$

The constant of integration C is determined by equating intensities at the boundary $r = R$, which we may do if we neglect losses due to refraction and reflexion.

We find

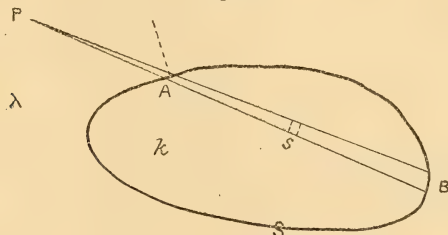
$$C = s e^{-\kappa R} e^{\lambda R},$$

so that

$$I_{\lambda} = \frac{s}{r^2} e^{-\kappa R} e^{-\lambda(r-R)}. \quad . \quad . \quad . \quad . \quad (3)$$

§ 2. *The Cosine Law of Emission.*—We do not have to look far for an immediate application of (3). Radiations from incandescent bodies emanate in practically all cases from a volume distribution of vibrating elements.

Fig. 2.



Thus, if we have an incandescent body bounded by a surface S, radiations from the vibrating elements in an element of volume dv in the interior are practically all absorbed before reaching the surface at A and thence an observer at P. If κ be the coefficient of absorption of the incandescent body to its own radiations, the intensity at P (situated outside S in a medium of coefficient of absorption λ) due to a single vibrating element at s is, from (3),

$$\frac{s}{r^2} e^{-\kappa R} e^{-\lambda(r-R)},$$

where $R = As$ and $r = Ps$.

If there are N vibrating elements per unit of volume, the

intensity at P due to radiations from an element of volume dv is

$$dI = Ns e^{-\lambda r_1} e^{-\kappa(r-r_1)} \frac{dv}{r^2},$$

where $r_1 = PA$.

If dv refer to an element of volume cut out by the intersection of spheres of radii r and $r+dr$, and centre at the vertex P of a small cone of solid angle ω , we have

$$dv = r^2 \omega dr.$$

The total intensity at P per unit cross-section normal to PA due to contributions from all the elements in the solid angle ω is

$$I = Ns\omega e^{-\lambda r_1} \int_{r_1}^{r_2} e^{-\kappa(r-r_1)} dr, \text{ where } r_2 = PB,$$

or

$$I = \frac{Ns\omega}{\kappa} e^{-\lambda r_1} \{1 - e^{-\kappa(r_2-r_1)}\}. \quad (4)$$

In an actual case λ is the coefficient of absorption for air, which is very small, so that we may take $e^{-\lambda r_1}$ to be unity. The exponential term $e^{-\kappa(r_2-r_1)}$ represents the fraction of radiation which can penetrate the entire thickness AB. In solid incandescent bodies whose thickness is large compared with a wave-length this fraction is negligible.

Thus the intensity at P is given very approximately by

$$I = \frac{Ns\omega}{\kappa}, \quad (5)$$

i. e. the intensity per unit cross-section of the radiation contained in a small solid angle ω viewed in any direction PA is proportional to the solid angle ω . This is equivalent to stating that the whole surface S appears uniformly bright. Under these conditions we may replace the volume-distribution of radiating elements by a distribution of intensity over the surface S. If dS be an element of surface at A cut out by the cone ω , and ϕ the angle between PA and the normal at A, we have

$$dS = \frac{\omega r_1^2}{\cos \phi},$$

so that (5) takes the form

$$I = \frac{Ns}{\kappa} \frac{dS \cos \phi}{r_1^2};$$

i. e. if I_0 be the normal intensity at unit distance contributed

by the element dS , we have the familiar form of the *Cosine Law*

$$I = I_0 \frac{\cos \phi}{r_1^2} \dots \dots \dots (6)$$

§ 3. In cases where the cosine law of emission fails we conclude that it is not legitimate to replace the volume distribution of vibrating elements by a surface distribution over the boundary. We must, therefore, examine departures from the cosine law in the light of the more complete expression (4). We notice first of all that for incandescent bodies for which κ is considerable, practically all the radiation which reaches P comes from a very thin surface-layer, perhaps only a few wave-lengths in thickness. We are therefore justified in neglecting effects of reflexion and refraction at the boundary, since these can hardly obey the optical laws in so thin a transition layer.

Formula (4) shows us to some extent on what conditions the efficiency of a radiating surface depends. Practically all actual means of exciting radiations in an incandescent body depend on maintaining an expenditure of energy throughout the entire volume, while the only portion of the body which contributes to the intensity of the radiation at an exterior point is an excessively thin surface-film. If it were possible to concentrate the same amount of energy throughout this thin exterior film, we should expect a considerably higher efficiency. It seems probable that the high efficiency of the phosphorescent light emitted by glow-worms and fire-flies may depend on just such a surface-concentration of energy, due in this case to chemical transformations at the boundary.

It seems remarkable that the *Cosine Law of Emission* should not have hitherto been presented in the light of absorption theory. Fourier*, in his memoir on 'Heat,' cites a reference to one of his earlier papers, in which he probably deduced the law along lines just given. It will be noticed from (5) that the total intensity inside a cavity in an infinite solid, or at any rate in one bounded by an exterior surface so large that contributions from portions near the exterior are small compared with those from portions near the cavity, is given by

$$I = 4\pi \frac{Ns}{\kappa}.$$

I is independent of the shape and size of the cavity, and

* Fourier, 'Chaleur,' Paris, 1822, p. 31, Chap. 1. The paper referred to is in *Mém. Acad. des Sc.* tome v., Paris, 1826, pp. 179-213.

also of the position of P in its interior. This result is employed by Fourier as a verification of the cosine law *.

§ 4. In deducing the formula just given, we have employed the simple exponential law of absorption

$$I = I_0 e^{-\kappa x}.$$

This by itself involves a violation of the principle of conservation of energy. In the case of gases, we know that absorption of light is accompanied by lateral scattering according to the well-known Rayleigh law. In the case of incandescent solids the problem is very much more complicated. Each of the radiating elements, besides being subject to a primary disturbing cause, is also subject to the aggregate radiation from all the other elements in the surface S. This constitutes what Schuster† has called "Radiation in a Foggy Atmosphere." The complete expression of this problem can be given in terms of an *integral equation* in three dimensions. This, together with some applications to the intensity of skylight, the writer hopes to communicate in a future paper.

XX. *Absorption Problems in Radioactivity.* By LOUIS VESSOT KING, B.A. (Cantab.), Lecturer in Physics, McGill University ‡.

[Plate VII.]

§ 1. **T**HE intensity of β - and γ -rays in their passage through matter decreases approximately according to the exponential law

$$I = I_0 e^{-\kappa x}, \quad (1)$$

I_0 being the intensity at an arbitrary origin $x=0$ as measured by the ionizing power of the rays, and κ the coefficient of absorption. Under these conditions it can easily be shown that the intensity at a distance r from a point-source of rays in a medium whose coefficient of absorption is κ is given by

$$I = \frac{s}{r^2} e^{-\kappa r}, \quad (2)$$

s being the intensity at unit distance when there is no absorption.

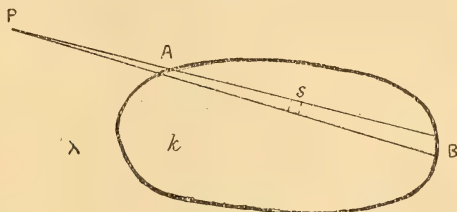
* Fourier, *loc. cit.* p. 31, § 47.

† Schuster, *Astrophysical Journal*, Jan. 1905, p. 1.

‡ Communicated by Prof. H. T. Barnes, F.R.S.

If, then, we have a mass of radioactive matter enclosed by a surface S , the intensity of the primary radiations which reach P can be easily calculated, as in the corresponding optical case*. The intensity at P due to contributions from

Fig. 1.



the mass cut out by a small cone PAB of solid angle $d\Omega$ is given by

$$dI = Ns d\Omega e^{-\lambda r_1} \int_{r_1}^{r_2} e^{-\kappa(r-r_1)} dr,$$

where N is the number of radioactive molecules per unit volume, λ the coefficient of absorption for air, κ that for the radioactive mass itself, while $r_1 = PA$, $r_2 = PB$, and $r = Ps$.

The total intensity as measured by the ionization per unit volume in an electroscope at P is given by

$$I = \int \frac{Ns}{\kappa} e^{-\lambda r_1} \left\{ \int_{r_1}^{r_2} e^{-\kappa(r-r_1)} dr \right\} d\Omega, \quad \dots (3)$$

the integral being taken so as to include contributions from all the elements of the radioactive mass.

We notice that if the radioactive molecules are distributed uniformly in the mass S and if S is homogeneous we have

$$I = \frac{Ns}{\kappa} \int e^{-\lambda r_1} \{1 - e^{-\kappa(r_2-r_1)}\} d\Omega. \quad \dots (4)$$

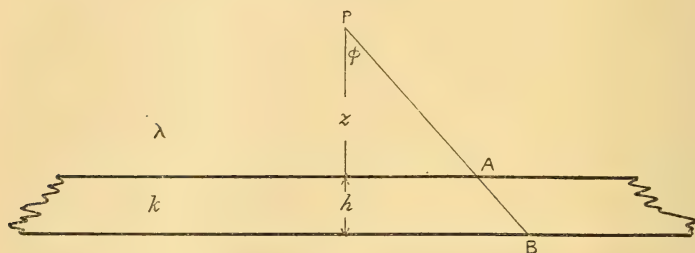
In this form (4) leads to a curious reciprocal relation which may be stated as follows:—The ionization per unit volume at P due to a distribution of N molecules per unit volume throughout a mass occupying a surface S , is equal to the total ionization throughout S due to N molecules of radioactive matter concentrated at P .

* King, "Note on the Cosine Law of Radiation," *supra*, p. 237.

§ 2. Absorption in Flat Plates.

In most cases (4) leads to integrals which are difficult to evaluate numerically. A case of considerable interest and one for which the integrals reduce to tabulated functions is afforded by considering the γ -radiation from a homogeneous distribution of radioactive matter throughout an infinite slab of thickness h .

Fig. 2.



Let z be the height of P above the surface of the plate, ϕ the angle which PA makes with the perpendicular from P , ψ the azimuth angle which the plane through PA and the perpendicular makes with a fixed direction in the plane of the slab. We then have $r_2 - r_1 = AB = h / \cos \phi$, $r_1 = PA = z / \cos \phi$, and $d\Omega = \sin \phi d\phi d\psi$.

Thus (4) gives on integrating with respect to ψ between 0 and 2π ,

$$I = \frac{2\pi N s}{\kappa} \int_0^{\pi/2} e^{-\lambda z \sec \phi} \{1 - e^{-\kappa h \sec \phi}\} \sec \phi d\phi. \quad (5)$$

We note that the integral

$$\int_0^{\pi/2} e^{-x \sec \phi} \sin \phi d\phi = x \int_x^{\infty} \frac{e^{-u} du}{u^2},$$

by the transformation $\cos \phi = \frac{x}{u}$; integrating by parts,

$$\int_0^{\pi/2} e^{-x \sec \phi} \sin \phi d\phi = e^{-x} - x \int_x^{\infty} \frac{e^{-u} du}{u}.$$

The last integral

$$\int_x^{\infty} \frac{e^{-u} du}{u} = - \int_{-\infty}^{-x} \frac{e^u du}{u}$$

has been tabulated by Glaisher* who writes

$$\int_{-\infty}^{-x} \frac{e^u}{u} du = Ei(-x).$$

We thus have, denoting the integral by $f(x)$,

$$f(x) = \int_0^{\frac{\pi}{2}} e^{-x \sec \phi} \sin \phi d\phi = x \int_x^{\infty} \frac{e^{-u} du}{u^2} = e^{-x} + x Ei(-x). \quad (6)$$

We note that

$$\begin{aligned} \int_0^{\phi} e^{-x \sec \phi} \sin \phi d\phi &= x \int_x^{x \sec \phi} \frac{e^{-u} du}{u^2} \\ &= x \int_x^{\infty} \frac{e^{-u} du}{u^2} - \cos \phi x \sec \phi \int_{x \sec \phi}^{\infty} \frac{e^{-u} du}{u^2} \\ &= f(x) - \cos \phi f(x \sec \phi). \quad (7) \end{aligned}$$

From (6) the function $f(x)$ is easily tabulated by the use of tables of the exponential functions and of the exponential integral. A short table of values of the function $f(x)$ is given below. The results are shown graphically on Plate VII. fig. 1, with a curve of the function e^{-x} added for comparison.

TABLE I.

Table giving the values of e^{-x} and $f(x) = e^{-x} + x Ei(-x)$.

x .	e^{-x} .	$f(x)$.	x .	e^{-x} .	$f(x)$.	x .	e^{-x} .	$f(x)$.
0	1.0000	1.0000	1	.9048	.7225	1.3	.2725	.0964
.0001	.9999	.9990	2	.8187	.5742	1.4	.2466	.0839
.001	.9990	.9927	3	.7408	.4691	1.5	.2231	.0731
.01	.9900	.9497	4	.6703	.3894	1.6	.2019	.0638
.02	.9802	.9131	5	.6065	.3266	1.7	.1827	.0558
.03	.9704	.8817	6	.5488	.2762	1.8	.1653	.0488
.04	.9608	.8535	7	.4966	.2349	1.9	.1496	.0428
.05	.9512	.8278	8	.4493	.2009	2.0	.1353	.0375
.06	.9418	.8040	9	.4066	.1724	3.0	.0498	.0106
.07	.9324	.7819	1.0	.3679	.1485	4.0	.0183	.0032
.08	.9231	.7610	1.1	.3329	.1283	5.0	.0067	.0010
.09	.9139	.7412	1.2	.3012	.1111	6.0	.0025	.0003

* Glaisher, Phil. Trans. 1870, p. 367. An abridged table of the Exponential-Integral, $Ei(-x)$, is given in Dale's 'Five-figure Tables of Mathematical Functions,' Arnold's, London, 1908. Extensive tables of the integrals

$$\int_x^{\infty} \frac{e^{-u} du}{u^2}, \quad \int_x^{\infty} \frac{e^{-u} du}{u} = Ei(-x), \quad \int_x^{\infty} u e^{-u} du \quad \text{and} \quad \int_x^{\infty} u^2 e^{-u} du,$$

to 9 significant figures at intervals of .001 between $x=0$ and $x=1$, and at intervals of .01 between $x=1$ and $x=2$, have been published by W. Lash Miller and T. R. Roseberg in the 'Transactions of the Royal Society of Canada,' 2nd series, vol. ix. 1903, sect. iii. pp 73-107.

When x is small we have

$$Ei(-x) = \gamma + \log x - x + \frac{x^2}{2 \cdot 2!} - \frac{x^3}{3 \cdot 3!} + \&c.$$

where γ is Euler's constant, $\gamma = .5772$.

Thus the expansion for $f(x)$ when x is small is

$$f(x) = 1 + x \log x - (1 - \gamma)x - \frac{x^2}{2} \dots \quad (8)$$

When x is large the asymptotic expansion for $f(x)$ is easily found from (6) by successive partial integrations to be

$$f(x) = \frac{e^{-x}}{x} \left\{ 1 - \frac{2!}{x} + \frac{3!}{x^2} - \dots \right\}. \quad (9)$$

Returning to (5) we see that the intensity at a distance z from the slab is given by

$$I = \frac{2\pi Ns}{\kappa} \left\{ f(\lambda z) - f(\lambda z + \kappa h) \right\}. \quad (10)$$

§ 3. This result has an immediate application to the theory of the decrease with height above the earth's surface of the intensity of the penetrating radiation in the earth's atmosphere, a problem considered by Eve*, who has worked out the case for a homogeneous distribution of radioactive matter (radium) throughout an infinite depth. With a slight change in notation the result is there obtained in the form

$$n = \frac{2\pi Q n_0}{\kappa} \int_1^\infty e^{-\frac{\lambda z}{v}} dv, \quad (11)$$

where

- n = number of ions produced per second per c.c.,
- $Q = 2.7 \times 1.4 \times 10^{-12}$ gramme per c.c. = the mean radium content for sedimentary rocks (*Strutt*).
- $\kappa = .034 \times 2.7 \text{ cm.}^{-1}$ = mean coefficient of absorption of γ rays by rocks (*McClelland*).
- $n_0 = 3.74 \times 10^9$ = number of ions produced per c.c. per sec. in air at normal temperature and pressure at a distance of 1 cm. from 1 curie of radium supposed concentrated at a point (absorption of γ rays by air and by the substance of the radium salt neglected) (*Eve*)†.
- $\lambda = .000044 \text{ cm.}^{-1}$ = coefficient of absorption of γ rays by air at normal pressure and temperature‡.

* Eve, "On the Ionization of the Atmosphere due to Radioactive Matter," *Phil. Mag.* xxi. Jan. 1911, pp. 26-46.

† Eve, *Phil. Mag.* Oct. 1911, p. 551.

‡ Hess, "Ueber die Absorption der γ -Strahlen in der Atmosphäre," *Phys. Zeit.* xii. Nov. 1911, p. 998. A mean value of $\lambda = 447 \times 10^{-4}$ is obtained, in substantial agreement with the value employed by Eve.

If we write $Ns=Q$, and $h=\infty$ in (10), and notice that $f(\infty)=0$, we have

$$n = \frac{2\pi Q n_0}{\kappa} f(\lambda z). \quad . \quad . \quad . \quad . \quad (12)$$

The integral

$$\int_1^\infty e^{-\frac{\lambda z}{v}} dv = \lambda z \int_{\lambda z}^\infty \frac{e^{-u}}{u^2} du = f(\lambda z),$$

so that (12) agrees with the result obtained by Eve.

By means of (10) we may compare the effect of surface layers of radioactive matter of different depths in their influence on the gradient of intensity of penetrating radiation. If we take the intensity at the surface $z=0$ as unity, we have to calculate the fraction

$$\frac{f(\lambda z) - f(\lambda z - \kappa h)}{1 - f(\kappa h)},$$

for various values of z and h . It is more convenient, in the use of tables, to calculate the above fraction for various values of λz and κh . Then, by employing the values of λ and κ given in Eve's paper, we can find the corresponding values of z and h . In the following table a few values of the gradient due to layers of different thicknesses are given. The height above the earth's surface (z) is expressed in metres, the thickness of the layer of radioactive matter (h) is expressed in centimetres, and the intensity at the earth's surface is in each case taken as unity.

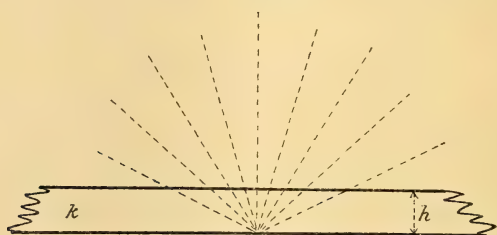
TABLE II.

z metres.	λz .	$h=11$ cm. $\kappa h=0.1$.	$h=1.1$ cm. $\kappa h=0.1$.	$h=11$ cm. $\kappa h=1.0$.	$h=\infty$ $\kappa h=\infty$.
0	0	1.000	1.000	1.000	1.000
11.4	.05	.472	.706	.812	.828
22.7	.1	.340	.535	.696	.722
45.5	.2	.239	.379	.543	.574
67.2	.3	.178	.288	.437	.469
114	.5	.109	.182	.297	.327
159	.7	.078	.123	.214	.235
227	1.0	.050	.073	.131	.148

The results are shown graphically in Plate VII. fig. II. These curves show very distinctly that even in the case of distribution of radioactive matter throughout an infinite thickness, practically the whole effect on the gradient is due to a layer very little more than 11 cm. thick. This point is of some importance in an actual measurement of the gradient. Unless the penetrating radiation is measured over a fairly level and homogeneous area, we cannot expect (12) to give an adequate representation of the gradient*.

§ 4. It is interesting to notice that a considerable number of absorption problems for flat plates involve the exponential integral. Several such problems are considered by Soddy†.

Fig. 3.



The results (due to Sir J. Larmor) are given for a point-source of radium in contact with a plate of thickness h . In the notation of the present paper the ratio of the total radiation over an angle of 180° on the opposite side of the plate to that which would exist if the plate were removed is given by

$$\frac{I_h}{I_0} = e^{-\kappa h} + \kappa h Ei(-\kappa h) = f(\kappa h).$$

If the radiation be confined to a cone of semi-vertical angle θ , we have

$$\frac{J_h'}{J_0'} = \frac{f(\kappa h) - \cos \theta f(\kappa h \sec \theta)}{1 - \cos \theta}.$$

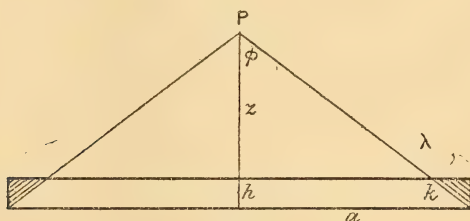
* Cf. Wulf, *Phys. Zeit.* Sept. 15, 1910, p. 811.

Hess (*loc. cit.*) finds from observations taken during a balloon ascension that there is no appreciable diminution in the intensity of the penetrating radiation with height as far as 1000 metres. From the remarks of the present section it would appear that a comparatively small amount of solids containing radioactive matter (*e. g.* sand-ballast &c. taken up in the car) might give rise to enough penetrating radiation to mask the effect due to height above the earth's surface.

† Soddy (F. & W. M.) and Russell, "The Question of the Homogeneity of γ -rays," *Phil. Mag.* xix. May 1910, p. 725.

These results follow from the solutions of the problems already considered by making use of the reciprocal theorem stated at the end of § 1 of the present paper. This theorem explains how the two different types of absorption problems lead to the same mathematical expressions.

Fig. 4.



It is perhaps not without interest to notice that the intensity at a point on the axis of a circular slab containing a distribution of radioactive matter can be evaluated. The result is easily obtained from (5) by taking the integrals from 0 to ϕ instead of from 0 to $\frac{\pi}{2}$, ϕ being the angle subtended by the radius a of the plate at P. Then by (7) we obtain for the ionization at P,

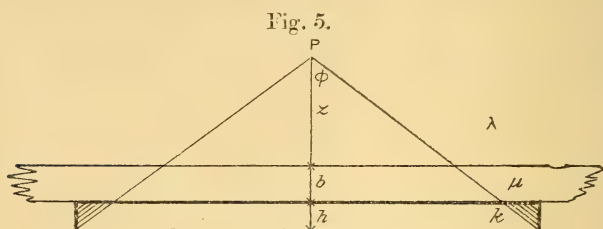
$$n = \frac{2\pi Q n_0}{\kappa} \left[f(\lambda z) - f(\lambda z + h\kappa) - \cos \phi \left\{ f\left(\frac{\lambda z}{\cos \phi}\right) - f\left(\frac{\lambda z + h\kappa}{\cos \phi}\right) \right\} \right]. \quad (13)$$

This result neglects the contribution of the ring generated by the revolution of the shaded area in the figure around the axis of the slab. This will be negligible if the radius be large compared with h , and P be not too close to the plate.

If we have a screen of absorbing matter, thickness b , coefficient of absorption μ , interposed between P and the circular plate, the intensity at P is given by the formula

$$n = \frac{2\pi Q n_0}{\kappa} \left[f(\mu b + \lambda z) - f(\mu b + \lambda z + h\kappa) - \cos \phi \left\{ f\left(\frac{\mu b + \lambda z}{\cos \phi}\right) - f\left(\frac{\mu b + \lambda z + h\kappa}{\cos \phi}\right) \right\} \right]. \quad (14)$$

We may perhaps notice that the screening effect of the slab (b, μ) is independent of its position between P and the



active slab, as far as the primary rays are concerned. Formula (14) is of considerable generality, and includes all the results already given.

XXI. *On a Method of Investigating the Transpiration of Gases through Tubes.* By JOSEPH H. T. ROBERTS, M.Sc., University of Liverpool*.

THE study of the transpiration of a gas through tubes affords a means of determining the viscosity, and thus of investigating certain of the molecular properties of the gas. The earliest systematic observations on gaseous transpiration were those of Graham †; but since the discovery in 1860 ‡ of Maxwell's law of the independence of viscosity and pressure, in virtue of which the viscosity of a gas is deducible from its transpiration coefficient, numerous experimenters have adopted this method for the determination of gaseous viscosities. The most expeditious way to find the viscosities of a number of gases is to determine the coefficient absolutely for one of them, and to deduce the coefficients for the others from a comparison of their transpiration times under the same circumstances.

With a view to the fulfilment of the latter condition some observers have used a maintained vacuum for the removal of the transpired gases; this, however, is not only unnecessary, but undesirable, as the transpiratory behaviour then becomes complicated with the effusive, and only with very long tubes can the one be considered to be separate from the other. Another objection to the use of the vacuum is that, if the higher pressure be comparable with that of the atmosphere, the transpiration tube requires to be very long to ensure normal flow. Indeed, Graham in some cases used capillaries 22 feet in length (made by fusing together shorter pieces), his results only becoming concordant for tubes above a certain relative length.

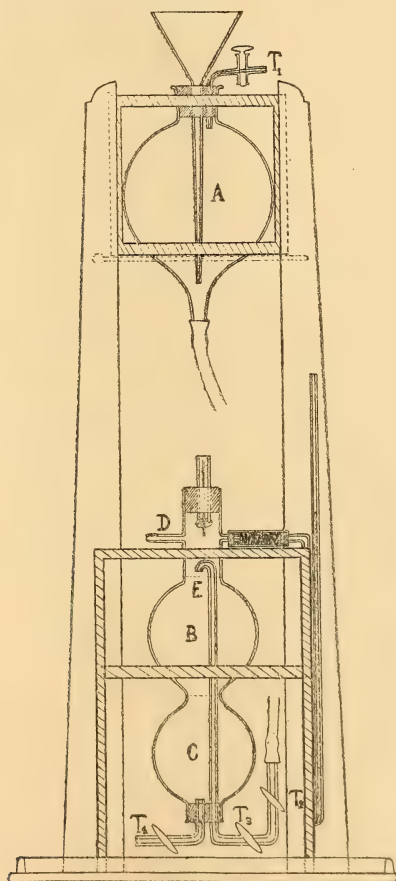
* Communicated by Prof. L. R. Wilberforce.

† Phil. Trans. 1846, 1849.

‡ Phil. Mag. 1860.

Considerable simplification is introduced, however, if the transpired gases be allowed to escape into the atmosphere; pressures slightly in excess of that of the atmosphere may then be used, and short, uniform capillaries employed.

The pressure requires to be automatically kept constant by a device which does not interfere with the accurate measurement of the volume transpired. For this purpose it is desirable to allow the transpiration of a constant volume of gas, and to measure the volume between points at which the cross-sectional area of the vessel is small. These improvements are embodied in the apparatus to be described, which will be found very convenient in practice and has the advantage of being readily constructed.



The apparatus consists of a mercury reservoir, A, provided with the usual constant-pressure device; the stem of the

funnel constitutes the air-tube, the funnel and the tap T_1 are hermetically sealed into the reservoir, and the tap T_1 is closed after the reservoir is filled with mercury. The carriage containing the reservoir is supported in a strong wooden tower, about 3 feet in height, and rests upon horizontal iron bars, placed in holes at any desired height.

The lower glass vessel consists of two spherical parts B, C (diameters about 9 and 8 cm. respectively), which are filled with the gas to be experimented upon, the gas being supplied, through drying-tubes, to the side tube D. The other side tube leads to a manometer, which should contain some liquid giving off little vapour: Fleuss pump-oil may be used for lower pressures, and mercury for higher pressures.

The upper end of the vessel is closed by a well-fitting rubber stopper, through which passes a short length of glass tubing, about 5 mm. bore; at the upper end of this tube is a small piece of rubber tubing which can be closed to exclude air until an experiment is begun. This is important, as the presence of a very small amount of foreign gas has a considerable effect upon the transpiration time*. The capillary is contained within this glass tube, and is secured at its lower end with soft wax.

The tap T_2 is to turn the mercury absolutely on or off, T_3 is to regulate the rate of inflow, and T_4 is to empty the vessel after an experiment. The mercury passes up the curved tube E, and enters the vessel at a fixed height, and therefore at a constant rate, once the pressure inside the vessel has become constant; the gas is forced through the capillary tube, and its pressure is indicated on the manometer. The tap T_2 being full on, T_3 is adjusted until a suitable pressure is obtained within the vessel, and everything is allowed to attain a steady state; with the dimensions given, this state will be attained before the mercury reaches the lower part of bulb B; the time is then observed for the mercury to pass marks at the lower and upper ends of bulb B, the volume between the marks being determined subsequently.

If the adjustment of the tap T_3 be preserved, and the mercury again passed through, the rate of inflow of the mercury, and of the efflux of the gas, will be practically the same as before, for pressures on the manometer which are small compared with the statical pressure due to the mercury. Thus the pressures required to force different gases through the same capillary at the same rate can be at once compared.

The dependence of pressure upon length for a constant

* Graham (*loc. cit.*).

rate of flow, and the influence of end-effects, can be examined by using successively smaller and smaller portions of the same capillary, the tap T_3 being fixed in position throughout.

To compare the transpiration rates for different gases under the same circumstances, a single capillary is used for all the gases. The time of transpiration of the gas is first found for a moderate pressure, and then, using air, an adjustment of T_3 is made to give the same pressure on the manometer. A trial adjustment is made with air to suit the pressure obtained with each gas; and thus the various gases, being compared with air, can be compared with one another. The particular pressure taken is immaterial, as the ratio of the transpiration times of different gases under the same circumstances depends only upon the gases*. This ratio is the ratio of their viscosities, and hence if the viscosity of air be known, the viscosities of other gases can be obtained by comparison.

The theory of these experiments, which are obviously similar to those carried out by Poiseuille and Hagen on the behaviour of water and other liquids in passing through a capillary tube, may be easily developed by the analogy of the theory of these hydraulic experiments. This theory† leads in the case of gases to a law of speed which corresponds fully with that found by Poiseuille for liquids, and like the latter can be used to calculate the numerical value of the coefficient of viscosity from the measured amount of the gas transpired.

If p_1, p_2 be the pressures at the ends of the tube, V_1 the volume entering, V_2 the volume leaving per unit time, and μ the coefficient of viscosity, then

$$p_1 V_1 = p_2 V_2 = \frac{(p_1^2 - p_2^2) \cdot \pi \cdot r^4}{16 \mu l}.$$

For another gas under the same circumstances

$$p_1 V'_1 = p_2 V'_2 = \frac{(p_1^2 - p_2^2) \pi r^4}{16 \mu' l},$$

whence

$$\frac{V'_1}{V_1} = \frac{\mu}{\mu'},$$

$$\text{or} \quad \frac{t}{t'} = \frac{\mu}{\mu'},$$

where t, t' are the transpiration times for a given volume.

* Graham (*loc. cit.*).

† Meyer, *Pogg. Ann.* 1866.

From these equations the viscosity can be calculated directly or by comparison.

It will be seen that only a small quantity of gas is required for use with this apparatus, as the bulb C avoids the necessity for preliminary experiments: gases soluble in water can be used, and the volume of gas transpired can be measured very accurately. The vessel B should be bedded firmly in its socket, otherwise its sinking, as it fills with mercury, will cause an increase in the pressure-head.

This apparatus was first designed by Prof. Wilberforce and constructed here, being originally used by Mr. R. H. Albery for a series of observations on the effusion of gases through holes in thin plates; the writer has performed a large number of experiments with it, and found it very convenient in practice. In reproducing the apparatus care must be taken that the bulb C is not made too small, otherwise the steady state will not be attained before the mercury reaches the lower mark; for the adjustment of T_3 a preliminary experiment will then be necessary in every case, and one of the chief advantages of the apparatus will be lost.

An idea of the behaviour of the apparatus may be obtained, in conclusion, from the following figures. The capillary tubes used varied in length from 281 mm. to 10 mm., and in radius from 0.2504 mm. to 0.0964 mm., the radii being measured in the microscope.

In several experiments at pressures of 37.8 cm. of oil (density 0.873) the pressure varied by 1 mm.; in others at the same pressure the variation was imperceptible, and in some at a pressure of 32.3 cm. it varied by less than 1 mm. To show the reliability of the regulator T_3 a time of 56 seconds was taken six times with variation not greater than 0.3 second, and a time of 75.5 seconds was obtained six times within the same variations.

The following illustrates a good set of readings for a direct determination of the viscosity of air:—

Mean pressure of barometer	741.0 mm.
Mean pressure of manometer in mm. of } oil (density 0.873).....	274.2 mm.
Volume of air transpired	347.0 c.c.
Time taken.....	242.0 seconds.
Effective length of capillary	21.20 cm.
Mean radius	0.280 mm.
Mean temperature.....	11° 75 C.

From these data the direct determination of the viscosity of air gives

$$\mu = .000180.$$

The following table gives the viscosities deduced from a comparison of transpiration times : the same conditions do not hold throughout, but only for each comparison.

Gas.	Mean Ratio of Transpiration time to that of Air.	Mean Temp.	μ .
Air	Direct calculation.	11°·75 C.	·000180
Hydrogen	48·5 101·0	12°·25 C.	·0000864
Carbon dioxide...	60·8 75·5	12°·60 C.	·000145
Coal-gas	56·0 75·5	12°·90 C.	·000133

I take the opportunity of thanking Professor Wilberforce for constant interest and advice, in this and in other work.

George Holt Physics Laboratory,
University of Liverpool.

XXII. *Photo-Electric Fatigue.* By J. ROBINSON, M.Sc.,
Ph.D., Demonstrator in Physics at the University of Sheffield*.

SOME very interesting results on photo-electric fatigue were given by H. Stanley Allen in the Phil. Mag. for October 1910. He showed that the fatigue takes place practically at the same rate in darkness as in light, that it is independent of the electric field, but that the size of the vessel used has an influence on it. Some results which are brought forward in the following seem at first sight contradictory to those of Allen. To understand these differences, it will be necessary to consider closely the conditions under which the different experiments were made.

Allen polished his plates immediately before an experiment, and measured the photo-electric currents at atmospheric pressure directly afterwards, making measurements at regular intervals. He found the current to diminish with the time, and the rate of diminution to be independent of light.

In the present experiments, the electrodes were polished by rubbing with steel, and inserted in a glass vessel which was pumped out to a high vacuum as quickly as possible. The experiments were made under these conditions, and extended

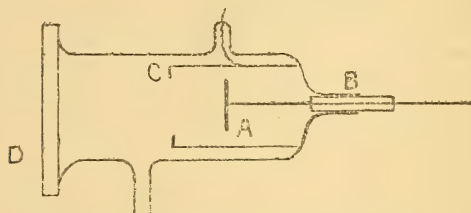
* Communicated by the Author.

over some weeks, during which time the vacuum was constantly maintained.

The general arrangement of the apparatus was as follows:—

The electrode A was insulated by an amber rod B, which was fastened by sealing-wax into the glass vessel. C is an

Fig. 1.



earthed metal tube with a hole in it to let the light through. The vessel was closed by a quartz plate D. Three different sources of ultra-violet light were used on different occasions, two quartz-mercury lamps, and an aluminium spark*.

Experiments were made to investigate whether there is a fatigue due to the action of ultra-violet light, and whether such fatigue depends on the electric field.

Experiments with a Zinc Electrode.

The electrode was connected to one pair of quadrants of a Dolezalek electrometer. When ultra-violet light falls on the zinc, the latter charges positively. The electrode was insulated and allowed to charge itself up positively under the action of light, and its potential at definite intervals noted. Firstly, this rate was measured when the light was allowed to fall on the electrode which had been in the dark for a long time, and was in a condition which will be described as fresh. Secondly, light was allowed to fall on the electrode for a certain length of time, say 5 minutes, after which time the rate of charging was measured as before. Thirdly, light was allowed to fall on the electrode for 5 minutes, but electrons were prevented from leaving the electrodes during this time by keeping it charged to a positive potential. Then it was insulated, and the rate of charging measured as before.

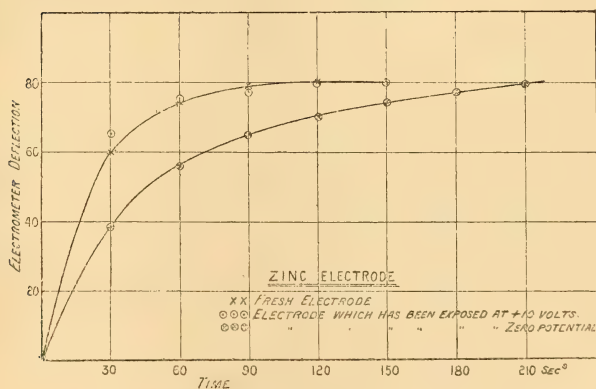
* The experiments were made partly at the Armstrong College, Newcastle-on-Tyne, and partly at the University of Sheffield.

TABLE I.

Fresh Electrode.		Electrode after being exposed to light for 5 minutes at +10 volts.		Electrode after being exposed for 5 minutes at Zero Potential.	
Time.	Charge.	Time.	Charge.	Time.	Charge.
30 secs.	60	30 secs.	65	30 secs.	38
60 "	74	60 "	75	60 "	56
90 "	79	90 "	77	90 "	64
120 "	79	120 "	80	120 "	70
		150 "	80	150 "	74
				180 "	77
				210 "	79

This table and the corresponding curves (fig. 2) show that the rate of charging of the zinc electrode is the same

Fig. 2.



throughout for the fresh electrode, and when it has been exposed to light but maintained at a potential of 10 volts positive. When the electrode was exposed to ultra-violet light at zero potential its rate of charging was diminished, or, in other words, the electrode was fatigued.

Aluminium Electrode.

Similar measurements were made with an aluminium electrode.

TABLE II.

Fresh Electrode.		Fatigued Electrode after exposure to light for 5 minutes.		Recovered Electrode after rest of 5 minutes.	
Time.	Charge.	Time.	Charge.	Time.	Charge.
15 secs.	176	15 secs.	58	15 secs.	176
30 "	201	30 "	86	30 "	206
45 "	220	45 "	101	45 "	218
60 "	230	60 "	114	60 "	234
90 "	241	90 "	130	90 "	250
135 "	254	120 "	145	120 "	261
180 "	260	180 "	166	180 "	269
240 "	271	240 "	179	240 "	274
360 "	271	300 "	196	300 "	274
420 "	271	360 "	208	360 "	278
		420 "	215	420 "	278
		480 "	224	480 "	280
		540 "	233	600 "	286
		600 "	235		
		660 "	239		
		720 "	245		

Fig. 3.

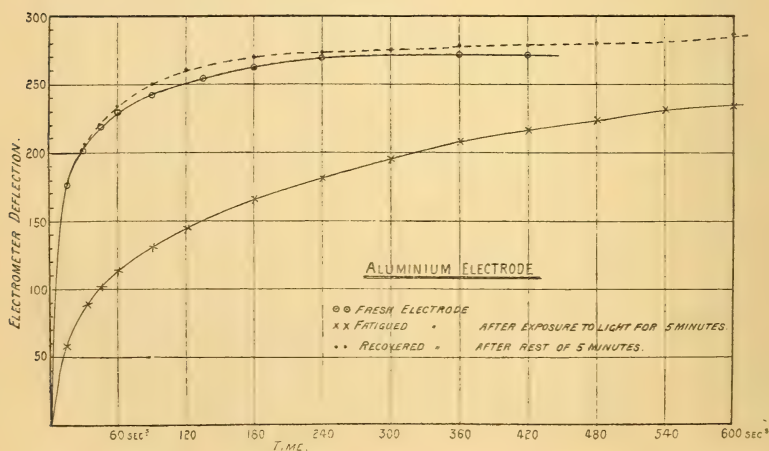


Fig. 4.

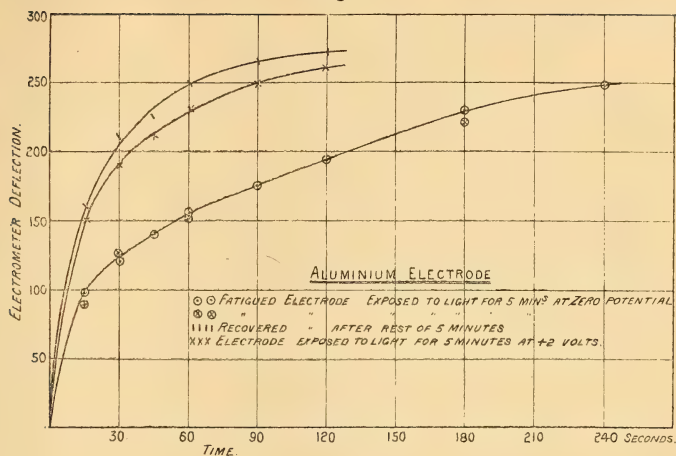


TABLE III.

Electrode after being exposed to light for 5 minutes at Zero Potential.		Recovered Electrode, after a rest of 5 minutes.		Electrode after being exposed to light for 5 minutes at +2 volts.		Fatigued Electrode, after exposure to light for 5 minutes at Zero Potential.	
Time.	Charge.	Time.	Charge.	Time.	Charge.	Time.	Charge.
15 secs.	100	15 secs.	160	15 secs.	150	15 secs.	90
30 "	120	30 "	210	30 "	190	30 "	125
45 "	140	45 "	225	45 "	210	45 "	140
60 "	155	60 "	250	60 "	230	60 "	150
120 "	195	90 "	265	90 "	250	90 "	175
180 "	230	120 "	272	120 "	260	120 "	195
240 "	248					180 "	220

These tables and curves for aluminium show the same characteristics as those for zinc.

Experiments of a different nature were also made to test the same points for aluminium. These were to measure the photo-electric currents under different conditions. The current was measured by joining the quadrants of the electrometer through a very high resistance, thus using the electrometer as a galvanometer. The current was measured, 1st, for the fresh electrode, 2nd, after it had been exposed to light for

some time at zero potential, and, 3rd, after it had been exposed at a positive potential.

TABLE IV.

Condition of Electrode.	Current.
Fresh.....	42
After an exposure to light for 5 minutes at a potential of +10 volts	42
After an exposure to light for 5 minutes at zero potential.....	13
Recovered Electrode	42

TABLE V.

Condition of Electrode.	Current.
Fresh.....	40
Exposed to light for 1 minute	25
Rest of 7 minutes	42
Exposed for 2 minutes	18
Rest of 5 minutes	41
Exposed for 3 minutes	18

TABLE VI.

Condition of Electrode.	Current.
Fresh.....	88
Fatigued for 5 minutes (at zero potential)	34
Recovered for 5 minutes	68
Fatigued for 5 " 	34
Recovered for 1 " 	51
" 2 " 	58
" 3 " 	63
" 5 " 	71
" 11 " 	78

The general results of these experiments are (1) that a metal is fatigued by exposure to ultra-violet light ; and after

the light is shut off it begins to recover its original activity again, only becoming fresh again after a few minutes; (2) that the metal is fatigued only when it gives off electrons under the action of ultra-violet light.

Thus there is a real photo-electric fatigue, *i. e.* one due to the action of light, as opposed to that fatigue observed by Allen.

The result that the fatigue is only observable when electrons are emitted is worthy of some little consideration. Hallwachs* considered a number of possible causes of photo-electric fatigue, and came to the conclusion that the chief cause is the gas occluded in the metal. The kind of fatigue that he investigated was of a similar nature to that mentioned by Allen. A possible explanation of the results of this paper can be obtained on Hallwachs's view. When the electrons leave a metal there will be a steady stream of them from a certain depth of the metal, and it is fair to suppose that some of them will bring molecules of the occluded gas to the surface, thus increasing the amount of gas there for the time being. For these electrons, giving rise to the photo-electric effect, which have a small velocity, gas has a large absorption coefficient†; so that as the gas accumulates at the surface fewer electrons can get through, thus accounting for the decrease in the photo-electric current. On the other hand, when the electrons cannot leave the metal, by having the latter charged positively, there will be no stream of electrons to the surface, and so no accumulation of gas there.

The explanation of the recovery of the photo-electric current on this view is that the gas will diffuse from the surface either back into the metal or out of the metal, when the light is shut off, leaving the gas in the metal uniformly distributed over it.

Some support of the above view is given by the fact that very thin electrodes which have been in a vacuum for some time show no photo-electric fatigue. This has been shown for thin aluminium leaf and for a very thin deposit of platinum on quartz.

A point which needs further consideration is why the particles of gas when carried to the surface of the metal by the electrons do not leave the metal altogether, instead of accumulating there. One may consider that there is some surface effect to account for this. Hallwachs has discussed such a possibility, and tried experimentally, but without

* *Ann. der Phys.* xxiii. p. 459 (1907).

† Lenard, *Ann. der Phys.* xii. p. 714 (1903); Robinson, *Ann. der Phys.* xxxi. p. 809 (1910).

success, to establish some relation between photo-electric fatigue and contact potential *. Lenard † came to the conclusion some time ago that such a surface-layer must exist. The following experiments seem to argue in favour of the existence of such a layer.

It was found that the final positive potential taken up by the zinc electrode under the action of light was by no means constant. Starting with it at the same potential as the metal cylinder surrounding it, *i. e.* earthed, its potential as registered by the deflexion of the electrometer-needle rose rapidly at first, after the light was put on, and then rose much more slowly (fig. 2). The typical form of the curve can be divided into these two parts, of rapid rise and of slow rise. In all curves, the first part was always of the same form, but the second part varied very much, especially if the light was allowed to fall on the metal for a long time. Sometimes it remained parallel to the axis of time for some minutes and then commenced to rise; at other times it increased gradually all the time, and sometimes it increased very slowly at first and then suddenly began to rise rapidly. It might be mentioned that this was also found to be the case when monochromatic light was used, so that the light was of small intensity.

A satisfactory explanation of this has not been attempted, but very probably it has something to do with a double layer at the surface of the metal.

The conclusions to be drawn from this paper are entirely different from Allen's. Here a real photo-electric fatigue has been observed. The point to be considered in connexion with Allen's results is whether the main thing he investigated was photo-electric fatigue, or whether the fatigue he observed was merely of secondary importance, occurring as a result of some other effect. Very possibly the surfaces of his electrodes were not in a stable condition just after polishing, and some sort of readjustment of the surface sets in immediately. This would occur quite independently of the action of light or of the electric field. A similar phenomenon has been observed by the present writer. When quartz-fibres are made conducting by depositing a metal on them from a cathode in a discharge-tube, the electrical resistance of the fibre varies very much after coming into the atmosphere. When the fibre is coated with platinum the resistance increases with the time, and when it is coated with copper it may become

* *Loc. cit.*

† *Ann. der Phys.* xii. p. 449 (1903).

an absolute insulator again after a few hours. There is possibly some connexion between this alteration of resistance of thin films and the photo-electric fatigue mentioned by Allen, and some experiments are being made at present to test it.

I have great pleasure in recording my best thanks to Professor Stroud, of the Armstrong College, Newcastle-on-Tyne, and to Professor W. M. Hicks, of the University of Sheffield, for the use of the apparatus necessary for the above experiments.

XXIII. *The Electron Theory of Contact Electromotive Force and Thermoelectricity.* By O. W. RICHARDSON, *Professor of Physics, Princeton University* *.

THE following method of deducing certain formulæ which connect some of the physical properties of conductors, particularly in the domain of thermoelectricity, with the number and state of the free electrons present in them, is a natural development of considerations which the writer put forward some time ago in order to account for the laws which regulate the emission of negative electrons from hot bodies †. The method is based on two fundamental assumptions. The first, which is common to all forms of the electron theory of metallic conduction, is that the electric current in metals is carried by electrons which move about freely, exert a pressure, and are otherwise dynamically equivalent to the molecules of a gas. The second is that the potential energy of an electron is much less when it is inside an uncharged conductor than when it is extracted and removed to a considerable distance. It follows that a definite amount of work w has to be done by an electron before it can escape from a conductor, and it is the force at the interface, which corresponds to this amount of work, which retains the electrons in the conductor at ordinary temperatures.

This position has recently been strengthened by an accumulation of experimental evidence. It has been found to give an adequate quantitative explanation of the number of electrons emitted by hot bodies under different conditions. The emitted electrons have been found to have a distribution of velocity in accordance with the requirements of Maxwell's law, and to have a mean translatory kinetic energy identical

* Communicated by the Author.

† Camb. Phil. Proc. vol. xi. p. 286 (1901); Phil. Trans. A. vol. cci. p. 497 (1903).

with that of a molecule of a gas at the temperature of the metal. By an application of the principles of the kinetic theory of gases it follows that the same statements are true of the free electrons *inside* the metal at the same temperature. Finally, the existence of the work w has been put on a firm basis by the discovery of the corresponding heating and cooling effects when electrons pass into and out of a metal.

Several of the calculations which follow have been given by the writer in a course of lectures on the electron theory of matter, in the past few years. It seems desirable to publish them apart as the results which have been obtained by other investigators in this subject are not in complete accordance, and a discussion of the differences sheds some light on the nature of the phenomena concerned. The strength of the present method lies in the fact that it is completely independent of the idea of free paths, and of the assumptions about the nature of collisions which play a prominent part in most forms of the electronic theory of conductors.

We shall suppose that all the free electrons are alike and negatively charged in order to simplify the calculations; although the method is equally applicable to the case in which different kinds of electrons, both positive and negative, are considered to be present. The view that there are several kinds of free electrons to be reckoned with can hardly be considered to have had much success so far in reducing the apparently rather considerable inconsistencies of the electron theory of conduction. In what follows very considerable use will be made of the theorem that in any system in equilibrium at a constant temperature θ , if n_1 is the concentration of the electrons at a point A and n_2 that at a point B then

$$\frac{n_2}{n_1} = e^{-W/R\theta},$$

where W is the work done in taking an electron from A to B and R is the gas constant in the equation $pv = R\theta$, reckoned for a single electron. This theorem* has been proved by writers on the kinetic theory of matter with a degree of generality which covers all the conditions contemplated in the electron theory of conductors.

We shall suppose each metal to be characterized by the possession of a number n of free electrons per unit volume. The value of n is different for different metals, and for a given metal it is a function of the temperature θ only. In

* Cf. Jeans, 'Dynamical Theory of Gases,' p. 78.

every case n is a very large number, so large that the fractional change in n produced by the communication of an electrostatic charge to a conductor of finite size is negligible in all practical cases. The largeness of n is of course deduced from the results of experiments interpreted by the light of the electron theory. The functions w which measure the work done by an electron in passing from the interior to the exterior of a conductor are also to be regarded as characteristic of each substance. They are functions of the temperature both explicitly and implicitly through n .

Intrinsic Potential Differences.

We shall begin by considering a vacuous enclosure surrounded by insulating walls maintained at a constant temperature θ . We shall also suppose that the thermionic emissivity of the material bounding the enclosure is so small that it may be disregarded. If an initially uncharged metallic conductor is placed inside such an enclosure it will emit negative electrons, the initial rate of emission being much greater the higher the temperature of the metal. Clearly this process will not go on indefinitely. The positive charge which the metal acquires, in virtue of the emission, tends to pull the electrons back, and ultimately a steady state is reached in which as many return as are emitted in a given time. This steady state will be accompanied by a statistically steady distribution of the external electrons, and also of the external electric potential. The theorem which we have already mentioned enables us at once to write down the relation between the concentration of the electrons n and n' at any two external points whose potentials are V and V' . It is

$$\frac{n}{n'} = e^{-\frac{\epsilon(V-V')}{R\theta}},$$

where ϵ is the charge on an electron. Since there is equilibrium between the electrons inside and outside the conductor we have further

$$\frac{n}{n_1} = e^{-\{w_1 + \epsilon(V - V_1)\}R/\theta},$$

where n and V correspond to any external point, as before, n_1 is the number of free electrons per cub.centim. inside the metal, V_1 is the potential at its surface, and w_1 is the work done by an electron in crossing the surface of the conductor from the interior.

Now suppose that there are two conductors of different materials present in the enclosure. As in the previous case, they are to be of considerable size, so that the electrons which they emit are small in number compared with those which are retained. For the present we shall also suppose that the two bodies are not in contact with each other. As before, the electrons in the two conductors and in the surrounding enclosure will ultimately reach a condition of statistical equilibrium, and the conductors will acquire definite potentials, which we may denote by V_1 and V_2 . Let W be the work done in taking an electron from the first to the second conductor when equilibrium has been established. Then

$$\frac{n_2}{n_1} = e^{-W/R\theta},$$

or

$$W = R\theta \log \frac{n_1}{n_2}.$$

But this work is also equal to

$$w_1 + \epsilon(V_2 - V_1) - w_2,$$

where the suffixes refer to the values of the different quantities for the two conductors. Hence

$$w_1 - \epsilon V_1 - R\theta \log n_1 = w_2 - \epsilon V_2 - R\theta \log n_2.$$

Similarly, if there are r conductors,

$$\begin{aligned} w_1 - \epsilon V_1 - R\theta \log n_1 &= w_2 - \epsilon V_2 - R\theta \log n_2 \\ &= \dots = w_r - \epsilon V_r - R\theta \log n_r. \end{aligned}$$

Thus the final state of equilibrium is characterized by the invariance of $w - \epsilon V - R\theta \log n$. This holds both for the internal and the external electrons, since $w=0$ for the latter.

The steady difference of potential $V_m - V_q$ between any two conductors m and q is evidently

$$V_m - V_q = \frac{1}{\epsilon} \left\{ w_m - w_q + R\theta \log \frac{n_q}{n_m} \right\}.$$

So far we have supposed all the bodies to be separate from each other, but the results are equally true if any number of them are in contact. To prove this it is necessary to consider the conditions which determine the state of equilibrium of the system more fully than we have done. Disregarding the electrons present in the surrounding space, which may be done here on account of the smallness of the external

pressures, it is evident that the state of the system is completely determined by the n variables $w_1 w_2 \dots w_n$, the n variables $n_1 n_2 \dots n_n$, and $n-1$ of the variables $V_1 V_2 \dots V_n$, one of which is arbitrary, together with the temperature θ . Now the $n-1$ equations of the type

$$w_m - \epsilon V_m - R\theta \log n_m = w_p - \epsilon V_p - R\theta \log n_p$$

are not the only equations connecting the $3n-1$ variables. We have seen that the w 's are functions of the n 's and θ , so that there are n equations of the type $w_p = f_p(n_p, \theta)$. In virtue of the equilibrium between the negative electrons and the positive remainder inside each conductor there are also n equations of the type $n_p = F_p(\theta)$. There are thus $3n$ variables and $3n-1$ equations, so that when θ is given all the n 's and w 's and the differences $V_m - V_q$ are determined. This is true independently of the relative position of the different conductors, and includes physical and electrical contact as a particular case. It is clear that

$$V_m - V_p = \frac{1}{\epsilon} \left\{ w_m - w_q + R\theta \log \frac{n_q}{n_m} \right\}$$

measures a true intrinsic difference of potential (contact electromotive force) between the conductors m and p .

The values of the electrical conductivity and some other considerations indicate that the number n of free electrons in unit volume is of the same order of magnitude for all the

metallic conductors, and the term $R\theta \log \frac{n_q}{n_m}$ is found to lead

to comparatively small electromotive forces of the order of magnitude of those required to account for the Peltier effect. So far no method has been devised for measuring the values of the w 's except at high temperatures, and the relation between any given w and the temperature is a matter of much uncertainty, so it is rather risky to argue from the values of the w 's at high temperatures to the values of these functions at ordinary temperatures. Broadly speaking, however, there is no doubt that the more electropositive metals have smaller values of w , and the differences which have actually been observed are of the order of magnitude which corresponds to the Volta effect. The fact that negative electrons are emitted at much lower temperatures from the alkali metals than from their more electronegative brethren strongly supports this view, since the concentration of the free electrons is much the same in all cases. It seems to

the writer that the balance of the evidence is now strongly in favour of the view that the Volta contact electromotive force is an intrinsic property of the pure metals, and not, as is perhaps more widely believed, an accidental development caused by traces of chemical action. At the same time there is no reason for doubting that the actual measured value of the contact electromotive force is very sensitive to actions of a chemical nature, as it should be on the view we have been discussing.

The case for the chemical origin of contact electromotive force rests largely on the results of a number of experiments which show that under certain circumstances, which are usually interpreted as involving the absence of oxygen or water-vapour from the surface films, the contact electromotive force, as measured by the condensing electroscope or an equivalent method, is found to either vanish or drop to a comparatively small value. The circumstances referred to are rather varied, and include boiling in heavy oil at about 140° C. (J. Brown *), exposure to the temperature of liquid air (Majorana †), and heating in a vacuum in the presence of drying agents (Spiers ‡, Greinacher §). In all these cases it seems quite likely that the surface of the metals under examination becomes covered with an insulating layer which entangles the escaping electrons. This would give rise to a double layer at the surface of each metal, and the seat of the whole of the potential difference between the metals would lie in these double layers. The surface of each metal would then act like a condenser positively charged on the metal side and negatively on the other. On separating the plates there would be no change in the capacity of the system and no free charges would be developed. An explanation along similar lines accounts for the null effects obtained by Greinacher by the ionization method. It seems quite clear that when the plates are immersed in insulating oil the apparent contact difference of potential will vanish on the electron theory. In the case of Majorana's experiment it is necessary to suppose either that a minute film of condensed moisture develops on the plates, or that the hydroxide films always present become non-conducting at the low temperatures. In any case a film a few molecules in thickness is all that is required. It is significant that Greinacher using the ionization method was unable to confirm Majorana's result. In

* Phil. Mag. [5] vol. v. p. 591 (1903).

† *Atti de Lincei*, vol. ix. p. 162 (1900).

‡ Phil. Mag. [4] vol. xlix. p. 70 (1900).

§ *Ann. der Physik*, vol. xvi. p. 708 (1906).

the cases in which the surface-films of gas are removed by heating it is to be expected that the oxide films which remain will be non-conducting, and this attitude is definitely supported by the fact that Greinacher was unable to get rid of the contact electromotive force by any kind of treatment when one of the metals tested was platinum, which is notoriously difficult to oxidize.

When two of the metals are joined by an electrolyte there will be no true equilibrium until the battery thus formed has run down, so that the potentials of the metals in the enclosure will not be the same as those they possess in the steady state. The present point of view does not, in fact, affect the thermodynamic theory of electrolytic cells, according to which their electromotive forces are determined by the heat generated by the chemical actions involved.

The Peltier Effect.

We shall now return to the case of two metals in contact. Consider the work done in taking an electron from one to the other in two ways: first, through the junction, and second, by crossing the outer surfaces. We thus obtain two equivalent expressions for the work P per unit charge, viz.

$$P = \frac{w_1 - w_2}{e} + V_2 - V_1 = \frac{R\theta}{e} \log \frac{n_1}{n_2}.$$

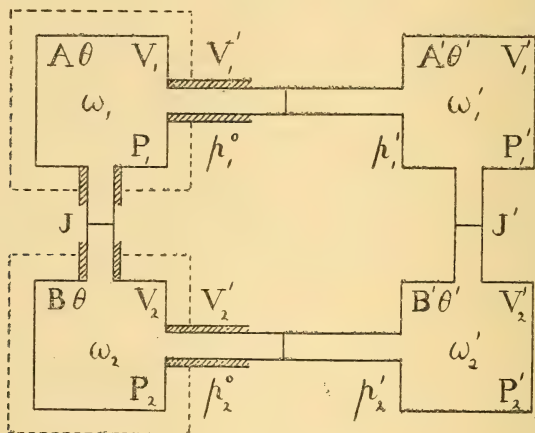
The second formula agrees with that given by J. J. Thomson* for the Peltier effect, but differs by a factor of two from the corresponding expression found by Drude†. Thomson's calculation is based on the idea that the electrons are in equilibrium under the opposing action of the electric force and the pressure gradient at the boundary, whereas Drude supposes a kind of convective equilibrium between the diffusion of the ions arising from the varying concentration and the electric currents arising from the balancing difference of potential. It seems to the writer that the standpoint taken by Thomson is much the safer of the two.

It does not seem quite certain, without further consideration, that the expression $\frac{R\theta}{e} \log \frac{n_1}{n_2}$ will represent the heating effect due to the passage of an electric current across the junction of two dissimilar metals, as the energy might conceivably be changed, partly or entirely, into some form other than heat. The fact may, however, be established by the

* 'Corpuscular Theory of Matter,' p. 74.

† *Ann. der Physik*, vol. i. p. 590 (1900)

following thermodynamic argument. Suppose that we have an electrical circuit made up of two metals A and B, such that the parts A and B with the junction J are maintained at the constant temperature θ , and A' and B' are at the constant



temperature θ' . The connexions between A A' B' and B may be imagined as being made by conductors of small cross-section protected by insulating covering when necessary for the argument. The connexions are removable when required, and the magnitude of the conductors A A' B' and B is supposed to be indefinitely large. Each conductor is surrounded by an insulating surface which does not absorb the electrons contained within it. A reversible cycle may be carried out by evaporating some definite quantity, let us say one gram molecule, of the electrons from A, condensing them at A', making them pass through the junction J' to B', evaporating at the surface of B', condensing at B, and returning through the junction J to A. In order to be sure that the cycle is reversible it is necessary to be careful about the way in which the electrons are transferred from A to A' and from B' to B. Of course as the different parts of the system are at different temperatures the state of each conductor will never be exactly that corresponding to thermal equilibrium at the specified temperature, but it may be made to approach that state with any desired degree of approximation by increasing the size of A A' B' and B in comparison with that of their connexions and the enclosure, the temperatures being maintained by contact over indefinitely large areas with electrical insulators kept at the specified temperatures. Under these circumstances the conductors will assume values of w , n , and

V which differ by indefinitely small amounts from the true equilibrium values at the specified temperatures. Thus in general the pressure p_1 , the temperature θ , and the electric potential V_1 of the electrons in equilibrium with A will all be different from the corresponding quantities θ' , p_1' , and V_1' of the electrons in equilibrium with A'. Let us suppose that $\epsilon V_1'$ is $> \epsilon V_1$. Around A place a screen (wire gauze) maintained at the potential V_1' and permeable to the electrons. This will reduce the pressure of the electrons outside of it to some definite value p_1^0 without affecting their temperature θ^* , and will reduce their potential to the value V_1' of the electrons in equilibrium with A'. The further transference of the electrons to A' will not involve any work against the electrical forces, and may be calculated on the hypothesis that the electrons are dynamically equivalent to a perfect gas †. The work done during the evaporation through the potential screen is $pv = NR\theta$ and the heat absorbed is

$$N(w_1 + \epsilon(V_1' - V_1) + R\theta),$$

where N is the number of electrons in one gram-molecule of them.

The freed electrons are then compressed adiabatically to a temperature θ' , the work done in this operation being $\frac{NR}{1-\gamma}(\theta' - \theta)$, where γ is the ratio of the specific heats of the electrons at constant pressure and constant volume. The heat absorbed in this operation is zero, but the pressure is changed from p_1^0 to $p_1'^0 \left(\frac{\theta}{\theta'}\right)^{\gamma/\gamma-1}$. We next expand to the pressure p_1' at constant temperature θ' . The work done is $-NR\theta' \log \frac{p_1'}{p_1'^0} \left(\frac{\theta}{\theta'}\right)^{\gamma/\gamma-1}$, and an equal amount of heat is absorbed. The electrons now have the same pressure, temperature, and potential as those in equilibrium with A', and the transference has been accomplished in a strictly reversible manner. They are then condensed into A', which is for the time being disconnected from the other conductors, at the constant pressure p_1' and temperature θ' . The work done in this operation is $-NR\theta'$ and the heat absorbed is $-N(w_1' + R\theta')$. The transference from A' to B' involves no work, but there is an amount of heat $-NP'e$ absorbed at the junction, where P' is the Peltier effect per unit charge. The electrons are then evaporated from B' at the equilibrium

* Cf. O. W. Richardson, Phil. Mag. [5] vol. xviii. p. 695 (1909).

† See below, p. 273.

pressure and temperature p_2' and θ' respectively, the work being $NR\theta'$ and the absorption of heat $N(w_2' + R\theta')$ *.

Next compress adiabatically to θ . The work is $\frac{NR}{1-\gamma}(\theta - \theta')$, the heat absorbed being nil. During this step the pressure is changed from p_2' to $p_2' \left(\frac{\theta'}{\theta}\right)^{\gamma/1-\gamma}$. Next expand at

constant temperature θ to the pressure p_2^0 , which is the equilibrium pressure at the potential screen around the conductor B. [We have assumed, for the sake of definiteness, that $\epsilon V_2' > \epsilon V_2$.] The work done and heat absorbed in

this step are each equal to $-NR\theta \log \frac{p_2^0}{p_2'} \left(\frac{\theta}{\theta'}\right)^{\gamma/1-\gamma}$. Now condense into B at θ and p_2^0 . The work is $-NR\theta$ and the heat absorbed is $-N(w_2 + \epsilon(V_2' - V_2) + R\theta)$. Finally, pass through the junction to A. The work here is nil, and the absorption of heat is NPe . The system is now in the state in which we found it, and the cycle of operations is reversible at every point.

The balance of work done during the cycle is

$$NR\theta' \log \frac{p_1^0}{p_1'} \left(\frac{\theta}{\theta'}\right)^{\gamma/1-\gamma} - NR\theta \log \frac{p_2^0}{p_2'} \left(\frac{\theta}{\theta'}\right)^{\gamma/1-\gamma}.$$

The heat communicated to the source is

$$N\{R\theta \log \frac{p_2^0}{p_2'} \left(\frac{\theta}{\theta'}\right)^{\gamma/1-\gamma} + w_2 - w_1 + \epsilon(V_1 - V_1' + V_2' - V_2) - Pe\}.$$

The ratio of these is equal, by the second law of thermodynamics, to $\frac{\theta' - \theta}{\theta}$; whence by virtue of the relations

$$R\theta \log p_1^0 = R\theta \log P_1 - w_1 - \epsilon(V_1' - V_1),$$

$$R\theta' \log p_1' = R\theta' \log P_1' - w_1',$$

$$R\theta \log p_2^0 = R\theta \log P_2 - w_2 - \epsilon(V_2' - V_2),$$

$$R\theta' \log p_2' = R\theta' \log P_2' - w_2',$$

$$R\theta' \log P_2' = R\theta' \log P_1' + w_2' - w_1' + \epsilon(V_1' - V_2'),$$

$$R\theta \log P_2 = R\theta \log P_1 + w_2 - w_1 + \epsilon(V_1 - V_2),$$

which determine the equilibrium between the electrons in the different parts of the system which are at the same

* When the nomenclature is not quite clear from the context it will be obvious after a glance at the diagram (p. 270).

temperature, if P_1 , P_1' , P_2 and P_2' are the pressures of the free electrons inside $AA'B$ and B' , we find that

$$Pe = R\theta \log \frac{P_2}{P_1},$$

showing that this expression or its equivalent $R\theta \log \frac{n_2}{n_1}$ is the true value of the cooling effect at the junction.

The Legitimacy of Applying the Gas Equation.

Objection to the results of the foregoing discussion may be urged on the score of the propriety of applying the equation of a perfect gas $pv = NR\theta$ to the electrons. At any rate the legitimacy of the application is not obvious without further consideration. It might be thought, for instance, that the pressure arising from the mutual repulsion of the electrons would seriously modify the simple equation, and that corrections would have to be introduced somewhat after the manner of Van der Waals's treatment of a real gas. It will be noticed, however, that the equation $pv = R\theta$ has only been applied to the external electrons, and the concentration of these is always exceedingly small at moderate temperatures. Now the correction for the work done by the mutual repulsion of the electrons depends upon the square of the concentration, and thus vanishes, in comparison with the external work, in the limit when the concentration is small. On the other hand, the size of the electrons is very much less than that of a molecule, so that the correction for the finite size of the particles will be infinitesimal. It seems, therefore, that at small concentrations a collection of electrons will exhibit a closer dynamical approximation to the ideal gas than will any real gas under comparable conditions.

The Thomson Effect.

The expression for Lord Kelvin's specific heat of electricity may be deduced by means of a thermodynamic cycle, similar to that already considered, but not quite so complicated. It is now necessary to consider only two conductors, A and A' , of the same material but with different temperatures, θ and θ' . They are joined by a thin conductor of the same material, down which there is, of course, a constant stream of heat. Let the potential outside A be V_1 and that outside A' V_1' , and let eV_1' be $> eV_1$. As before we surround A by a potential filter maintained at V_1' . The reversible cycle consists in evaporating the electrons from A through the potential filter, bringing them by reversible processes to the

same temperature and pressure as those outside B, condensing them at B, and allowing them to flow down the conductor back to A.

In evaporating from A the work done is $NR\theta$, and the heat absorbed is $N(w_1 + \epsilon(V_1' - V_1) + R\theta)$. The work during the adiabatic transformation from θ to θ' is $\frac{NR}{1-\gamma}(\theta' - \theta)$, the heat absorbed nil, and the pressure changes from p_1^0 to $p_1^0 \left(\frac{\theta}{\theta'}\right)^{\gamma/1-\gamma}$. The next step consists in expanding to the pressure p_1' at the constant temperature θ' . The work done here is $-NR\theta' \log \frac{p_1'}{p_1^0} \left(\frac{\theta}{\theta'}\right)^{\gamma/1-\gamma}$, and an equal amount of heat is absorbed. In condensing into A' at constant temperature θ' and pressure p_1' the work is $-NR\theta'$ and the heat absorbed $-N(w_1' + R\theta')$. The flow down the conductor from A' to A is not accompanied by the expenditure of work, but involves an absorption of heat

$$= +N\epsilon \int_{\theta'}^{\theta} \sigma d\theta,$$

where σ is the specific heat of electricity.

Applying the second law of thermodynamics in the form

$\int \frac{dQ}{\theta} = 0$, we have, for the entire reversible cycle,

$$\begin{aligned} \frac{N(w_1 + \epsilon(V_1' - V_1) + R\theta)}{\theta} - \frac{NR\theta' \log \frac{p_1'}{p_1^0} \left(\frac{\theta}{\theta'}\right)^{\gamma/1-\gamma}}{\theta'} \\ - \frac{N(w_1' + R\theta')}{\theta'} + N\epsilon \int_{\theta'}^{\theta} \frac{\sigma}{\theta} d\theta = 0, \end{aligned}$$

and since

$$R\theta \log p_1^0 = R\theta \log P_1 - w_1 - \epsilon(V_1' - V_1),$$

and

$$R\theta' \log p_1' = R\theta' \log P_1' - w_1',$$

we have

$$+ \epsilon \int_{\theta'}^{\theta} \frac{\sigma}{\theta} d\theta - R \log \frac{P_1'}{P_1} - \frac{R\gamma}{\gamma-1} \log \frac{\theta}{\theta'} = 0,$$

whence by differentiation with respect to θ

$$\sigma = + \frac{1}{\epsilon} \left\{ \frac{R\gamma}{\gamma-1} - R\theta \frac{\partial}{\partial \theta} \left(\log \frac{P_1'}{P_1} \right) \right\}$$

if P is the pressure of the internal free electrons at the point whose temperature is θ and P_1 is the value of the same quantity at a point whose temperature has a fixed value, say θ_1 . Since $P \propto n\theta$, the value of σ may also be written

$$\sigma = + \frac{1}{\epsilon} \left\{ \frac{R}{\gamma-1} - R\theta \frac{\partial}{\partial \theta} \left(\log \frac{n}{n_1} \right) \right\}.$$

This formula differs from those given by both Drude and J. J. Thomson in the articles referred to. In Drude's case the logarithmic term differs by a factor of 2, which arises in the same way as the difference in the expression he finds for the Peltier effect. There also seems to be a confusion of sign in the expression for the heat generated by the internal electric forces. When these changes are made his formula reduces to that of J. J. Thomson. Both writers seem to neglect the energy required to push the electrons against their own pressure as they flow along the unequally heated conductor. The formula which I have found may be deduced after the manner of J. J. Thomson's calculations if this is taken into account. For, consider the electrons present in the region between two isothermal (and also equipotential) surfaces whose temperatures are θ and $\theta + d\theta$ respectively. The internal (kinetic) energy of the electrons on entering at the surface θ is $C_v\theta$, and on leaving at the surface $\theta + d\theta$ is $C_v(\theta + d\theta)$. The work done by the electrons at entrance is $(pv)_\theta = R\theta$, and on the electrons at leaving is

$$(pv)_{\theta+d\theta} = R(\theta + d\theta)$$

The work done on the electrons by the electric forces within the surfaces is

$$R\theta \frac{d}{d\theta} (\log P) d\theta.$$

Thus the net loss of energy by the metal comprised within the surfaces, owing to the passage of this amount of electrons, is

$$\left\{ C_v + R - R\theta \frac{d}{d\theta} (\log P) \right\} d\theta,$$

so that

$$\sigma = + \frac{1}{\epsilon} \left\{ \frac{R\gamma}{\gamma-1} - R\theta \frac{d}{d\theta} \left(\log \frac{P}{P_1} \right) \right\},$$

in agreement with the previous result.

The value of γ lies between $1\frac{2}{3}$ and 1, so that the minimum value of the first term on the right-hand side is

readily calculated. This minimum value is in every case greater, and in nearly all cases much greater, than the measured values of σ . Thus it follows, as J. J. Thomson has already pointed out, that the two terms must be nearly equal to one another. If the electrons have no internal momentoids $\gamma = 1\frac{2}{3}$, and it is necessary that n the number of free electrons inside a metal should for most metals be nearly proportional to $\theta^{3/2}$. If, on the other hand, $\gamma = 1\frac{1}{3}$, which is another possibility, we should have to have $n \propto \theta^3$ nearly.

An expression* for σ equivalent to the above has been deduced by H. A. Lorentz, on the assumption that the colliding electrons behave like hard elastic spheres.

Thermoelectric Circuits.

Now return to the four conductors AA' B and B', of which A and A' are of the same material, as also are B and B', but the material nature of A and A' is different from that of B and B'. A and B are maintained at the fixed temperature θ_0 , and A' and B' at the fixed temperature θ' . The four conductors are connected together as before. Consider the transportation of a number N of electrons round the circuit thus formed, without leaving the metal. In this case the only work done on balance, if any, is that done against the electrical forces. This is equal to $NT\epsilon$, where T is the thermoelectromotive-force of the circuit. This must be equal to the net absorption of heat during the transference so that

$$NT\epsilon = N\epsilon P' - N\epsilon P + N\epsilon \int_{\theta_0}^{\theta'} \sigma_2 d\theta + N\epsilon \int_{\theta'}^{\theta_0} \sigma_1 d\theta,$$

where P' and P are the Peltier effects at the hot and cold junctions, and σ_2 and σ_1 are the specific heats of electricity in B and A respectively. Substituting the values of P' , P , σ_2 and σ_1 already obtained we find, after integrating by parts, that

$$T = \frac{R}{\epsilon} \int_{\theta_0}^{\theta'} \log\left(\frac{P_2}{P_1}\right) d\theta = \int_{\theta_0}^{\theta'} \frac{P}{\theta} d\theta,$$

where P_2 and P_1 are the pressures of the free electrons in B and A respectively at the temperature θ , and P is the Peltier effect at a junction formed of A and B at that temperature.

* Quoted by J. Königsberger und J. Weiss, *Ann. der Physik*, vol. xxxv. p. 43 (1911).

Furthermore

$$\frac{dT}{d\theta'} = \frac{R}{\epsilon} \log \frac{P_2'}{P_1'} = \frac{P'}{\theta'}.$$

Since $P_2 = nR\theta$ and $P_1 = n_1R\theta$, we have

$$\frac{dT}{d\theta} = \frac{R}{\epsilon} \log \frac{n_2}{n_1}.$$

Thus the relative concentrations of the free electrons in different metals may be obtained, at all temperatures, from a knowledge of their thermoelectric powers. Since $\frac{dT}{d\theta}$ is very nearly a linear function of the temperature for most pairs of metals, over a considerable range of temperature, it would seem that n_2/n_1 cannot, for any pair of metals, be represented as a power of θ , but must be of the form $Ae^{b\theta}$, where A and b are constants. This form may, however, only be an empirical approximation.

A theory of thermoelectric phenomena, stated by its author to be based on principles somewhat similar to those which underlie the present development, has just been published in the *Annalen der Physik* by Mr. K. Baedeker *. I am unable to agree with the results of Mr. Baedeker's theoretical calculations, which seem to involve a misconception of the principles which should underlie the applications of the laws of thermodynamics.

The Function w.

The nature of the work w , which an electron has to do in order to escape from a metal, is a matter of considerable interest. If the positive and negative electricity were indefinitely subdivisible, like the mathematical elements of an ideal fluid, then the sign of the work would reverse with the sign of the escaping charge. This follows since, if there were a part of w which did not reverse with the sign of the charge, it would have to depend on the square and other even powers of the latter, and could be made to vanish in comparison with the remainder if the charge were removed in sufficiently small amounts. In such a case w could only arise from a discontinuity in the electric potential at the surface of the conductor, and the natural means of explaining its existence would be to postulate the occurrence of an electrical double layer.

* *Ann. der Phys.* vol. xxxv. p. 75 (1911).

This argument does not apply if the electricity is present in the conductor in the form of electrons. The smallest quantity of electricity which can be removed at one step is finite and equal to the charge of one electron. There is thus always a part of the work done in removing an electron from an uncharged conductor which is proportional to e^2 . This difference between the potential energy of an electron inside and outside the metal may be figured as the work done by the electron against the attraction of its image in the conductor. This is not infinite, as in the ordinary electrostatic theory, because the volume density of the electrification in the ultimate atoms of positive and negative electricity is finite. Sir J. J. Thomson's view that the atoms are spheres of uniformly distributed positive electricity occupied by comparatively small negative electrons of charge e , comparable in number with the atomic weight of the atom, and having an equal total charge, leads to values of w comparable with those given by the results of experiments on the emission of electrons from hot bodies. There is thus no necessity to introduce electrical double layers to account for the existence of the w 's.

This discussion brings out the necessity for using great care in the employment of the terms electric force and electric potential in problems of this character. To obtain the difference of potential between two points A and B it is not sufficient to find the work done in taking an electron from A to B, and to divide the result by the charge e . The quantity thus obtained may differ not only in magnitude but even in sign from the value corresponding to the limit when e is made zero.

The variation of w with θ is a matter of considerable practical interest. If one supposes that the positive electricity in the conductor can be treated as though it were continuously and uniformly distributed throughout its volume, then it appears that w is comparable with e^2/b , where b is the radius of a sphere of the positive electricity which carries a charge e equal to that of the negative electron. From this rough view of the phenomena one would expect that w would diminish with rising temperature, its temperature coefficient being comparable with that of the linear expansion of the material. The experimental data available are inadequate to test this point satisfactorily.

Some further applications of the method which has been developed will be considered in a later paper.

Palmer Physical Laboratory,
Princeton, N.J.

XXIV. *On the Radium Content of Secondary Rocks.* By
ARNOLD L. FLETCHER, B.A., B.A.I., *Research Assistant*
to the Professor of Geology in the University of Dublin.*.

IT was suggested to me by Professor Joly that an investigation of the radium content of typical sedimentary rocks was desirable in view of the discrepancies between some of the published results,—his own more especially being in the mean higher than those of other observers generally,—and also on account of the small number of observations actually available.

An additional reason for now making such an investigation is to be found in the facilities for rapid determination which the method of fusion offers †. This method being also freer from the uncertainties and risks of error besetting other methods, might be trusted to afford correspondingly more reliable data. The geological importance of a sufficiently comprehensive knowledge of the radioactivity of common sedimentary rocks has already been pointed out §.

The experiments were carried out in the manner described by Professor Joly (*loc. cit.*) with the exception of slight unimportant variations in the relative quantities of chemical fluxes employed to meet the varying degrees of basicity met with between the different rock types.

Attention has been drawn to the fact that the complete disengagement of the imprisoned emanation depends of necessity to a large extent upon two conditions: an active chemical change and a correspondingly free evolution—with effervescence if possible—of carbon dioxide, involving therefore a mobile rock-melt.

Professor Joly has recorded how the acidification of his more basic and viscous rock-melts by the addition of a small quantity of boracic acid resulted in a reduction of the constant of one of his electroscopes by over 20 per cent., and this increased yield of emanation consequent upon acidification has been observed in dealing with sedimentary materials. For example, a Zechstein dolomite from Hartz

* Communicated by the Author.

I desire here to pay my grateful acknowledgments to the Royal Society, under whose grant the following experiments were performed as a preliminary to the further investigation of Plutonic and Volcanic rocks.

† Joly, "On a method of estimating the quantity of Radium in Rocks, Minerals, etc." *Phil. Mag.*, July 1911.

§ Joly, 'Radioactivity and Geology,' p. 45.

fused in a bed consisting of a mixture of 7 grams of borax and 20 grams of a mixture of sodium and potassium carbonates, showed a very markedly increased yield by the addition of radium-free boracic acid. Again, in the examination of the finer particles of a soil, the addition of about 15 grams of borax, conferring fluidity upon an otherwise typically "dry" melt, and accompanied by a greatly increased effervescence, raised the result by over four times in one case, and three times in another. It was found that fusion, even of an acid rock powder with borax alone as a flux, was not in the absence of free effervescence capable of completely deemanating the melt.

It was judged desirable to attempt to approximate throughout as regards fluidity and effervescence to the conditions under which the standardization experiments were performed, rather than to differentiate between the slightly varying constants obtained with different rocks, in view of the slight and very uncertain nature of these variations.

The above conditions do not appear to be always necessary in the case of the purer Calcareous rocks, and seven experiments failed to detect a connexion between fusion conditions and yield of emanation. The White Jura Limestone from Wurtemberg yielded the same low figure, viz. 0.3×10^{-12} gr. per gram for the radium content quite irrespective of wide changes in the chemical nature of the fusion mixture. Again, two experiments on a very pure chalk which yielded a very "dry" melt when simply fused with carbonates, showed no appreciable rise when twice repeated with the addition of boracic acid, although in the first instance the evolution of carbon dioxide was very slight and in the latter case extremely violent.

An explanation is probably forthcoming, in the early break up of the CaCO_3 molecule in this class of rocks before fusion temperature is attained, involving the liberation of all the emanation independently of questions of effervescence or melt fluidity. It was indeed found that the mere heating of a limestone without the admixture of any chemicals was sufficient to very largely deemanate the rock powder.

Chemicals involved.

A few experiments were made to ascertain the most efficient chemicals having regard to the most desirable conditions of the melt, attained subject to the conditions

under which the standardization of the electroscopes was effected. It was found that while both borax and quartz powder confer fluid properties upon the melt, accompanied by a brisk effervescence, the temperature required in the case of the former was much lower and the reaction likely therefore to be the more complete. The marked advantage in fact in working with a mixture of borax and boracic acid, added to the fusion mixture of carbonates, is that, effervescence taking place at a much lower temperature than with the use of pure silica, renders the prolonged attainment of high temperatures unnecessary and thus lengthens the life of the furnace.

Were the expulsion of the emanation of radium from a rock-melt a result attendant merely upon the attainment of a condition of high temperature and independent of any mechanical disturbance, we might expect a similar effect in the case of thorium. An attempt, however, to measure thorium by a measure of the emanation contained in air passed over a fluid rock-melt under undisturbed conditions yielded a negative result.

Purity of the Chemicals.

The relatively low quantities of radium contained in some of the rocks, and in particular in some of the limestones and dolomites examined (quantities involving an increase in the rate of collapse of the gold leaf of the order of 3 and 4 scale-divisions per hour), might have been easily masked by the presence of a very small amount of radioactive impurity in the chemicals, and rendered therefore a knowledge of their purity imperative.

To this end a series of six experiments were made. It had been observed previously on several occasions that the mere fusion of a mixture of sodium and potassium carbonates failed to exert any appreciable effect on the rate of collapse of the gold leaf. Fusion, however, of these carbonates with varying quantities of borax and boracic acid—causing a violent effervescence of the melt—produced on three successive occasions on two electroscopes a small but quite unmistakable, and steady gain of two scale-divisions per hour, involving the minute but almost certain presence of at least 0.04×10^{-12} gram Ra per gram of mixed carbonates. This effect has been observed by others, and an allowance was made in rock determinations. No radium could be detected in the borax glass or boracic acid used.

Notwithstanding the precautions which were taken, it is
Phil. Mag. S. 6. Vol. 23. No. 134. Feb. 1912. U

just possible that the conditions obtained in individual experiments were not always identical with all types of rocks, and that for the more basic carbonates examined a slightly higher constant should be used than that obtained as the mean result of many experiments varying but slightly from the average value 0.6. Should this be so, it would bring the general mean of nearly all the different rock-types examined into striking equality, in view of the fact that the uranium contained by them owes its inclusion to the widely differing causes which the varying nature of their origin involves.

Constants of the Electroscopes.

About twelve experiments in all were made proper to the constants of the two electroscopes used throughout. From the mean of these below, which were the most reliable and closely agreeing of the standardization experiments, the constants were chosen.

Experiments on the Constant of the first Electroscope.

Charge.	Constant.
Granite, with .003 mg Uraninite	0.62
" " .006 " " 	0.57
Granite with a granite-melt containing 1 mg. Uraninite	0.69
	MEAN <u>0.66</u>

Experiments on the Constant of the second Electroscope.

Charge.	Constant.
Granite with .007 mg. Uraninite	0.32
Granite with a granite-melt containing the Radium in 10 c.c. of a Standard Solution (Rutherford)...	0.73
	MEAN <u>0.53</u>

The following experiments of a comparative nature were made upon the constants.

Comparison of Electroscopes.	Scale of 1st Elec. in scale-divs. per hr.	Scale of 2nd Elec. in scale-divs. per hr.	Constant of 2nd Elec. assuming 1st to be 0.6.
By means of a granite repeatedly previously tested, yielding closely agreeing results	33	48	0.44
By means of the fusion of a granite powder	35	24	0.92
By means of the fusion of a granite powder	28	24	0.70
By means of the introduction of the same volume of radioactive gases drawn from below and near to the surface of the soil	21	21	0.60
By means of a Cretaceous Chalk	13.3	16.4	0.38
By means of a Cretaceous Chalk	12.5	16.1	0.3
MEAN			<u>0.56</u>

In these experiments, which on the whole are in fair agreement, the mean value of the constants appears to be about 0.6; the tendency both by direct and comparative experiment being slightly above that figure in the case of one electroscope ($C=0.66$) and slightly below it in the other ($C=0.53$).

The mean result of six comparative experiments on the assumption that 0.6 represented the constant of the first electroscope yielded for the second the figure 0.56. It was therefore considered that by taking 0.6×10^{-12} gram radium as equivalent to a gain of one scale-division per hour for both instruments, there would be no error on the side of excess, and in all probability this figure is as nearly correct as certain risks of error pointed out by Prof. Joly as unavoidably incurred in the use of uraninite as a standard will permit. It is, however, satisfactory to know that this was the figure arrived at for the constant of the electroscopes in numerous determinations on the standard aqueous solution of Prof. Rutherford. As additional testimony to the truth of this figure and of the improbability of any considerable source of error dependent upon "personal equation," we have the mean value of nine experiments performed by Prof. Joly on an electroscope of equal dimensions and identical in construction. This mean comes out as 0.64. Finally, the reliability of the electroscopes in their very slight diurnal variation renders it practically certain that the following results are in the great majority of cases within 10 per cent. of their true value, and in view of the number of results from which the mean value is calculated, the percentage error is in this case in all probability even below this figure.

The following results were obtained :—

Coarse Detrital Sediments.

Geological Period.	Type.	Locality.	Radium per gram.
Tertiary	Greenish Calcareous Sandstone.	Stettin.	$3\cdot5 \times 10^{-12}$ gram.
Cretaceous	Yellow Sandstone.	Wald.	1·7 " "
	Deister Sandstone.	Hanover.	1·5 " "
	Quader Sandstone.	Hartz.	1·7 " "
	Green Sandstone.	Ireland.	1·6 " "
	Green Sandstone.	Westphalia.	1·4 " "
	Green Sandstone.	Westphalia.	1·6 " "
	Reddish Wealden Sandstone.	Buckeburg.	1·7 " "
Triassic	Red Sandstone.	Odenwald.	0·8 " "
	Yellowish Bonebed Sandstone.	Brunswick.	1·4 " "
	Yellow Bunter Sandstone.	Vosges.	2·5 " "
	Red Bunter Sandstone.	Baden.	2·1 " "
Carboniferous ...	Dark Grey Sandstone.	Westphalia.	1·3 " "
	Yellowish Sandstone.	Westphalia.	1·6 " "
	Red Sandstone.	Vosges.	0·9 " "
	Sandstone *	Fifeshire from depth 1095 ft. Burnlip Bore.	0·5 " "
Devonian	Banded Sandstone.	New York.	1·4 " "
	Old Red Sandstone.	Ireland (Kildare).	0·4 " "
	Old Red Sandstone	Ireland (Dublin).	1·4 " "
	Yellow Sandstone (Fresh-water type).	Ireland (Kiltorean).	2·0 " "
	Greenish Grey Sandstone.	Trier.	1·9 " "
Pre-Cambrian ...	Red Torridonian Sandstone.	Scotland (Lough Craig).	0·8 " "
	Red Torridonian Sandstone and Quartz Conglomerate.	Scotland (Isle of Rum).	0·8 " "
Unknown	Diatomaceous Quartz Sandstone.		1·1 " "
MEAN... $1\cdot5 \times 10^{-12}$ gram.			

* A comparatively high result obtained from this rock was not substantiated.

Metamorphosed Sediments (coarse detrital).

Period.	Type.	Locality.	Radium per gram.
Permian	Compact Greenish Grey Greywackè.	Hartz.	2.0×10^{-12} gram.
	Granular Grey Quartzite.	Siebengebirge.	1.1 " "
	Muscovite Quartzite Schist.	Saxony.	1.5 " "
	Baked Sandstone.	Budingen.	None detected in 6.7 grams.
Devonian	Schistose Blackish Blue Quartzite.	Stadtwald.	4.0×10^{-12} gram.
	Schistose Grey Taunus Quartzite.	Nassau.	0.8 " "
	Greywackè.	Nassau.	2.7 " "
	Greywackè.	Ireland (Valentia).	0.6 " "
Pre-Cambrian	White Quartzite.	Scotland.	0.4 " "
MEAN... 1.5×10^{-12} gram.			

Argillaceous Metamorphosed Sediments (fine detrital).

Period.	Type.	Locality.	Radium per gram.
Triassic	Roofing Slate.	Rhine Provinces.	1.8×10^{-12} gram.
Carboniferous ...	Blue and White "Whet Slate."	Netherlands.	1.6 " "
	Clay Slate.	Ireland.	1.5 " "
	Burnt Slate.	Laacher See.	0.4 " "
Devonian	Blue Slate.	Valentia.	1.8 " "
	Dark Blue Killas.	Cornwall.	0.7 " "
	Clay Slate.	Hartz.	1.5 " "
	Red Clay Slate.	Nassau.	1.6 " "
Silurian	Green Phyllite.	Saxony.	1.6 " "
	Clay Slate.	Schneeberg.	0.9 " "
Ordovician	Dark Grey Shale.	Moffat.	1.1 " "
Cambrian	Red Slate.	Ireland (Dublin).	1.5 " "
	Red Slate.	Ireland (Dublin).	1.0 " "
	Red Slate.	Ireland (Wicklow).	1.3 " "
	Blue Roofing Slate.	N. Wales (Penrhyn).	0.7 " "
	Andalusite Slate.	Vogtland.	1.2 " "
MEAN... 1.3×10^{-12} gram.			

Mr. A. L. Fletcher *on the*
Calcareous Sediments.

Period.	Type.	Local ty.	Radium per gram.
Tertiary	Paludina-Limestone (Fresh-water).	Unknown.	0.7×10^{-12} gram.
	Nummulitic Limestone.	Unknown.	0.1 "
	Litorinella-Limestone (Fresh-water).	Rhine Provinces.	0.3 "
Cretaceous.....	Indurated Chalk.	Ireland (Galway).	0.3 "
	Limestone.	Westphalia.	0.9 "
	Limestone.	Westphalia.	1.2 "
	Limestone.	Westphalia.	1.5 "
	Chalk	Rügen.	0.8 " (mean of 4 results).
	(Erdiger Kalk).		
	Turonien Limestone. Serpulite Limestone.	Westphalia. Hanover (Deister).	None detected. 1.5×10^{-12} gram.
Jurassic	Yellowish Porous Limestone (Schaumkalk).	Brunswick.	1.1 "
	Spotted Grey Jura Limestone.	Saxony.	1.0 " (mean of 2 results).
	White Jura Limestone.	Wurtemberg.	0.3 " { Mean of 3 al- most identical results.
	Earthy Limestone. Lithographic Limestone.	Meudon. Solenhofen.	3.2 " " None detected.
Triassic	Crystalline granular Dolomite.	Saxony.	None detected.
Permian	Dolomite Flagstone (Plattenkalk).	Hanover.	0.2×10^{-12} gram.
	Zechstein Limestone (Bituminous Stinkstone).	Hartz.	1.7 "
	Zechstein Dolomite.	Hartz.	1.3 " (mean of 2 results).
Carboniferous.	Dolomitic Limestone (Earthy).	Ireland (Kildare).	1.2 "
	Limestone.	Ireland (Galway).	1.0 " (mean of 2 results).
Devonian	Granular Dolomite.	Eifel.	0.4 "
	Dolomitic Limestone.	Rhine Provinces.	0.4 "
Unknown	Coral Limestone.	Unknown.	0.8 "
MEAN... 0.8×10^{-12} gram.			

With regard to the radioactivity of the disintegrated surface materials themselves, several experiments were made upon soils from both the country around Dublin and from the centre of the city.

The following procedure was adopted. The soil was dried over a water-bath, then gently broken and disintegrated with the fingers, and finally sifted, and the ratio of the finer particles to the bulk determined. The coarser fragments, quartz pebbles, organic matter, &c. were rejected and only the finer material examined. In both cases, and particularly in the case of the city soil, much trouble may be caused by the presence of organic and carbonaceous matter, which should be first ignited, otherwise volumes of gases incomparable with the capacity of an ordinary electroscope will be evolved. The results given below express the radium content of the fine particles in one gram of the original soil as found *in situ*.

Surface Materials.

	Radium per gram of fine soil particles passing a "50" sieve.	Equivalent radioactivity of soil as found <i>in situ</i> .
Soil from near Milltown, Co. Dublin...	5.2×10^{-12} gram.	2.9×10^{-12} gr. per gr.
Soil from College Park, Dublin	2.8×10^{-12} gram.	1.3×10^{-12} gr. per gr.

The actual radioactivity of the soil inclusive of its coarser fragments will therefore slightly exceed this figure, though the radium content of the larger particles may be pre-supposed low. The subsoil in the case of the Milltown soil is fine yellow clay, and under the College park consists of gravel and sand.

Carbonaceous Rocks.

Orrell Coal No Radium detected in 19 grams.

In dealing with carbonaceous specimens by the furnace method, it is necessary, on account of the formation of a volume of carbon monoxide out of proportion to the volume of the electroscopes, to ignite the specimen first in the open, the residue being then put by for a full period of three weeks before actual examination. In the case, however, of the

sample of coal examined, the very finely divided nature of the ash might introduce a possible source of error in the imperfect retention of the accumulating emanation. The ash was in this case therefore mixed with the normal quantity (10 grams) of borax-glass used in each separate examination, and the whole fused until the ash was completely embedded in the borax. This was then coarsely broken, and stored for the full period of time to avoid any error in a time calculation of the emanation percentage present, which might arise consequent upon a partial emanation only having occurred in the process.

The borax containing the embedded ash would effervesce on fusion with the carbonate fluxes, and fairly represent in this respect a rock under the same conditions.

With regard to the altered sediments, there is no reason to suppose that those which have suffered from extensive regional or contact metamorphism should on that account show any departure from the normal in their contained radium, nor was this found to be the case in those examined below.

Schistose Metamorphosed Sediments (fine grained).

Rock.	Locality.	Radium in grams per gram.
Mica Slate	Freybourg.	1.7×10^{-12} gram.
Talc Slate	Delaware R.	1.9 "
Mica Schist	Wicklow County.	1.4 "
Mica Schist	Wexford County.	0.9 "
Grey Schist	Oban.	0.6 "
Primitive Schistose Gneiss containing Anhydrite. }	Simplon Tunnel.	2.0 "
Schiste Lustré	Simplon Tunnel.	0.5 "
Mica Schist (Calciferous) .	Simplon Tunnel.	0.8 "
Laurentian Mica Schist ...		0.3 "
	MEAN...	1.1×10^{-12} gram.

Specimens were examined also from some exposures near Dublin of the actual contact of the Leinster Granite with its overlying Silurian strata, to discover if possible any marked effect due to the actual contact of the granite mass. Sections of the sedimentary rock cut both parallel and perpendicular to the direction of compression from specimens taken from

different distances from the plane of contact, show clearly the gradation from a normal Quartzite in the proximity of the granite to a Quartziferous Mica Schist at the point of contact.

A detectable increase on the amount of radium present in the quartzite might have been reasonably inferred from the increasing quantity of halo-bearing and radioactively darkened biotite developed in it on approaching the granite, but this was not in fact found to be the case.

Section.	Radium in grams per gram.
A micaceous Quartzite, with quartz grains uniformly small and Biotite uniformly distributed. Poor cleavage.	0.6×10^{-12} .
A micaceous Quartzite, quartz grains larger, more Biotite developed in parallel bands, with some halos.	0.8×10^{-12} .
A Mica Schist, much Biotite developed in bands. Halos plentiful. Cleavage well developed along foliation planes. Abundant granular Quartz, arranged in streams.	0.7×10^{-12} .

As far as the evidence in the case of these experiments goes, there is no abnormal amount of radium which would give rise to measurable effect due to the close proximity of the invading granite-mass.

A somewhat similar experiment was made in the examination of a stratum of Cretaceous Chalk from Carrickfergus, in thickness about one inch, caught between two sills of basalt, rendered crystalline, and iron stained, by their action.

Rock.	Radium in grs. per gr.
Chalk (rendered crystalline)	0.4×10^{-12} .
Same, another estimation	0.4 „
Basalt Sills enclosing Chalk	0.7 „

It will be seen that in spite of having experienced extreme metamorphism, the figure obtained for the chalk does not measurably differ from the result (0.3) obtained on the

unaltered chalk from Co. Antrim, referred to in the table on the limestones. Any increase is perhaps hardly to be expected in view of the low radioactivity of the sill itself, but there has been probably no loss. The contact zone of limestone with granite was similarly examined in the case of a somewhat weathered specimen from Switzerland, with similar results.

Rock.	Radium in grs. per gr.
Limestone at contact	0.3×10^{-12} .
Granite at contact	0.7×10^{-12} .

A positive result was obtained, however, from examination of the contact zone of the altered Silurian Slates with the igneous intrusion in a hand-specimen from Glendalough, Co. Wicklow, when the following figures were obtained :—

Rock.	Radium in grs. per gr.
Greisen abutting	0.8
Schist	3.3

The mean radioactivity of the altered Silurian Schists of Leinster, based on two experiments, is about 1.1×10^{-12} —normal for its type. There is therefore a positive, if moderately small augmentation in this case, the more emphasized by the relative poorness of the Greisen in radioactive materials. The Schist itself shows not only the high thermal and dynamic metamorphic characters shown by all these Schists, but the development of such secondary minerals as tourmaline indicates a certain amount of pneumatolytic action involving the removal of some bodies from the igneous and their recrystallization in the sedimentary rock.

The intrusive rock is not petrologically similar to the main granite-mass, but rather a greisen, and shows in addition a band of alteration, and the production of abundant white mica. Biotite is absent. In view of its magmatically differentiated origin, a relatively high radium content might reasonably have been presupposed, and its deficiency in radium relative to the main granite-mass, whose mean by the fusion method is about 2×10^{-12} gr. per gram, is noteworthy,

Summary.

The outstanding features of these results are (with the exception of the calcareous rocks) the persistence of the radium in consistent and nearly identical quantity from one rock type to another, and, with the same exception, their almost unvarying sameness in rocks of one type. Practically speaking, all the secondary rocks with the exception of those of calcareous nature contain approximately the same quantity of radium per gram, as will be seen from the figures below, but the differences though small may, in view of the large number of individual experiments performed, be regarded as positive. An explanation of the lower quantities of radium contained in the less important calcareous rocks has been given by Professor Joly*, and the results were therefore in this instance anticipated.

Table of Mean Results.

Rock Type.	Number of expts. on which average is based.	Radium in grams per gram.
Coarse detrital Sediments	24	1.5×10^{-12} .
Coarse detrital Sediments (Metamorphosed) ...	9	1.5 „
Fine detrital Sediments (Argillaceous)	16	1.3 „
Fine detrital Sediments (Schistose)	9	1.1 „
Calcareous Sediments	24	0.8 „

It would be misleading to include the large number of calcareous rocks investigated in a general mean, because they actually comprise but a small percentage (estimated at almost 5 per cent.) of the general sedimentary rocks of the earth's crust. The mean of the remaining specimens, 58 in number, is say 1.4×10^{-12} gram per gram.

I have to thank Professor Joly for his unfailing interest and constant advice throughout the course of these experiments.

Geological Laboratory,
Trinity College, Dublin,
December, 1911.

* 'Radioactivity and Geology,' p. 51.

XXV. *The Growth of Radium C from Radium B.*
*By K. FAJANS, Ph.D., and W. MAKOWER, M.A., D.Sc.**

IT has recently been shown by Fajans † that the product RaC_2 , discovered by Hahn and Meitner ‡, has a period of 1.4 minutes and emits β rays and that the α rays from RaC cannot be ascribed either to RaC_2 or to an unknown product following it in the direct radioactive series. The conclusion was therefore drawn that α rays are emitted by RaC_1 , the product whose period is known to be between 19 and 19.5 minutes. It was also shown that RaC_2 could be obtained from RaC_1 by recoil only in minute quantities, whereas RaD is obtained by this method in an amount theoretically to be expected from an α -ray recoil. On this account Fajans concludes that RaC_2 is not in the direct line of disintegration products of radium between RaC_1 and RaD , but constitutes a side branch from the main series, so that RaC_1 may give rise on disintegration either to RaD or to RaC_2 .

There are some important questions arising out of this conclusion, and it is the object of this paper to answer them. In the first place, we have to find out whether the whole of the β radiation from RaC is due to RaC_2 or whether RaC_1 also emits these rays; in the second place, we have to investigate what proportion of the atoms of RaC_1 give rise to RaD and to RaC_2 respectively.

The method of experiment consisted in observing the rise and fall of activity of a plate coated with pure RaB obtained by recoil from RaA . If the activity is measured by hard β rays then, assuming that RaB emits only soft rays, and knowing that RaC emits some very penetrating rays, the activity should at first be nothing and gradually rise to a maximum as RaC is formed and then fall off with time. The exact shape of the curve will, however, depend on whether the β rays arise only from radium C_2 or from radium C_1 as well. In figure 1 are given the curves calculated for the two extreme cases; the curve A refers to the case in which RaC_1 alone emits β rays and is calculated from the formula

$$C_1 = \frac{\lambda_B B_0}{\lambda_{C_1} - \lambda_B} [e^{-\lambda_B t} - e^{-\lambda_{C_1} t}] \quad . \quad . \quad . \quad (1)$$

* Communicated by Prof. E. Rutherford, F.R.S.

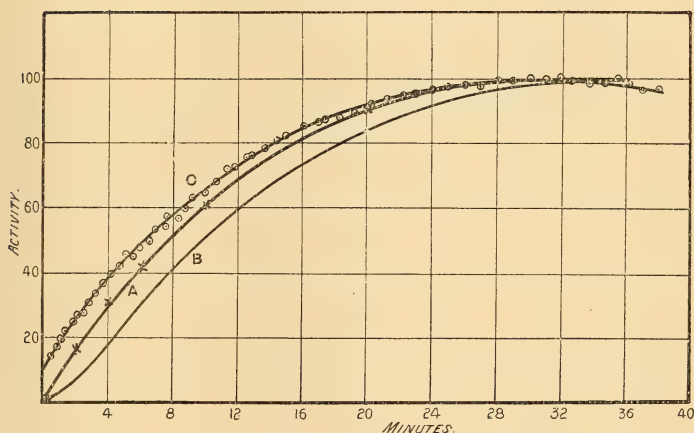
† K. Fajans, *Physik. Zeitschr.* xii. p. 369 (1911).

‡ Hahn and Meitner, *Physik. Zeitschr.* x. p. 697 (1909).

Curve B relates to the case in which RaC_2 alone emits β rays and is calculated from the formula

$$C_2 = \lambda_B \lambda_{C_1} B_0 \left[\frac{e^{-\lambda_B t}}{(\lambda_{C_1} - \lambda_B)(\lambda_{C_2} - \lambda_B)} + \frac{e^{-\lambda_{C_1} t}}{(\lambda_B - \lambda_{C_1})(\lambda_{C_2} - \lambda_{C_1})} + \frac{e^{-\lambda_{C_2} t}}{(\lambda_B - \lambda_{C_2})(\lambda_{C_1} - \lambda_{C_2})} \right].$$

Fig. 1.



The values taken in these equations are the following:—

$$\lambda_B = 4.33 \times 10^{-4} \text{ sec.}^{-1}$$

$$\lambda_{C_1} = 5.93 \times 10^{-4} \text{ ,,}$$

$$\lambda_{C_2} = 8.3 \times 10^{-3} \text{ ,,}$$

corresponding to the half-value periods of 26.7 and 19.5 and 1.4 mins. respectively.

It will be seen that the two curves obtained from (1) and (2) respectively differ appreciably from each other, and it is clear that if both RaC_1 and RaC_2 contribute to the radiation, a curve will be obtained lying between the curves A and B. It was therefore hoped by this method to find out whether RaC_2 contributes an appreciable share of the β radiation from RaC . The curves are so drawn that the maximum which occurs after 32.8 minutes is 100.

To carry out an experiment a plate was exposed in the usual manner in an electric field to radium emanation for a few minutes so as to collect on its surface a deposit of RaA . After removing the plate from the emanation, a second

collecting-plate was exposed as the negative electrode in an electric field to the recoil from the first plate for a few seconds so as to receive a deposit of RaB by recoil; the collecting-plate was then quickly transferred to a β -ray electroscope of the usual type and its activity measured at successive times through a thick aluminium screen, the thickness of which was varied in different experiments. The case of a screen 0.93 mm. thick is taken as typical and shown in figure 1, curve C, in which the time is reckoned from the end of the recoil.

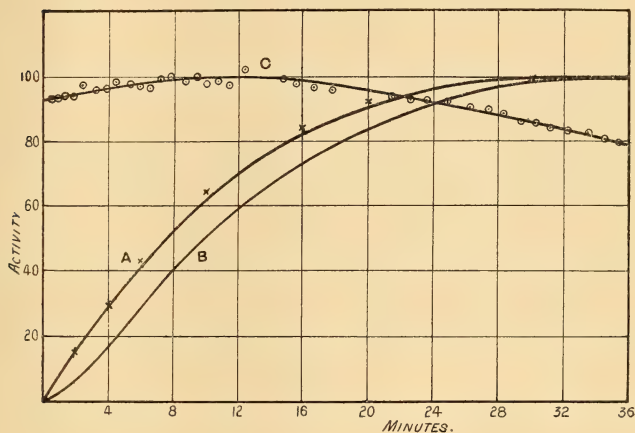
It will be noticed that the experimental curve does not coincide with either of the calculated curves; it lies above both curves and does not start from zero but from 10 per cent. of the maximum value. The cause of this discrepancy must in part be due to the fact that the collecting of the RaB by recoil did not occur instantaneously, but occupied 25 seconds. In this time a small quantity of RaC is formed and due allowance must be made in the curve for the RaC present at the beginning of the measurements; but the corrections to be introduced from this cause are too small to account for the observed differences. Thus a simple calculation shows that after an exposure of 25 seconds the quantity of RaC on the plate at time 0 is only 1.7 per cent. of the maximum after 32.8 minutes. As shown by H. W. Schmidt*, and as confirmed below, the remainder of the initial radiation is to be ascribed to RaB itself, which is thus seen to emit rays capable of penetrating 0.93 mm. of aluminium. Hence to obtain a curve showing the growth of activity of RaC from RaB it is necessary to subtract at each time, from the experimental values of the ionization, both the ionization due to the RaC originally present, which falls off with a period of 19.5 minutes, and the ionization due to RaB, which falls off with a period of 26.7 minutes. If this is done for the curve C and if the maximum value after 32.8 minutes is again taken as 100, a curve is obtained which coincides closely with the theoretical curve A, which was calculated on the assumption that RaC₁ was responsible for the major part of the radiation emitted by RaC. The points marked with crosses have been calculated in this way. It is therefore clear that RaC₂ does not contribute materially to the hard β radiation from RaC.

In order to extend the investigation to the case of the soft β rays emitted by RaC a similar experiment to that described above was made with an absorbing layer of aluminium

* H. W. Schmidt, *Annalen der Physik*, xxi. (1906).

0.09 mm. thick. The experimental curve is given in figure 2 C, and the curves A and B are the same theoretical curves

Fig. 2.



as those plotted in figure 1. It will be seen that the activity immediately after the recoil is more than 90 per cent. of the maximum activity. This is due to the existence of soft β rays emitted by RaB. If, however, corrections are applied to the experimental curve in a manner similar to that explained for the experiment on the hard radiation, a curve is obtained which again agrees very closely with curve A. It therefore appears that not only the hard radiation but also the soft radiation from RaC_2 contributes too small an amount to the ionization produced by RaC to be detected in these experiments. Now since the ionizing powers of successive products emitting β rays are of the same order of magnitude*, and since it has been shown by Fajans that RaC_2 emits β rays†, it follows from the above results, that the ratio of the number of atoms of RaC_2 to the number of atoms of RaC_1 in equilibrium is so small as to be incapable of detection in these experiments. This result is in good agreement with the conclusions arrived at by Fajans, that RaC_2 forms a side branch in the radium series and is not intermediate between RaC_1 and RaD, and that RaD is formed from RaC_1 in much greater quantity than RaC_2 .

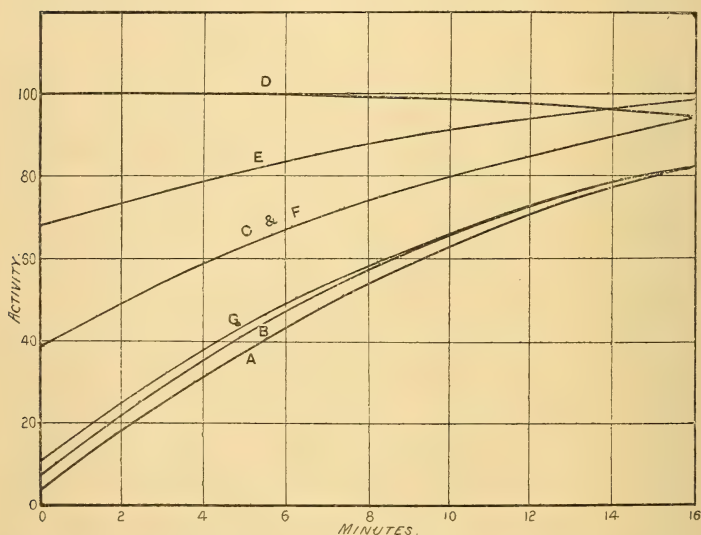
* Geiger and Kovarik, Phil. Mag. Oct. 1911.

† Fajans, *loc. cit.*

The Absorption of the β Rays of Radium B by Aluminium.

The above conclusions respecting RaC_2 depend on the assumption that when working with hard rays the initial activity of a surface coated with RaB is due to the emission of hard β rays from RaB. As has already been mentioned, such rays have been observed by H. W. Schmidt, but as the correctness of his results has been recently called into question by Hahn and Meitner*, it was necessary to investigate the matter more fully before any certain conclusions could be drawn regarding RaC_2 . For this purpose determinations with an ordinary β -ray electroscope were made of the rise and subsequent fall of the ionization produced by a plate coated with RaB when measured through different thicknesses of aluminium. Some typical curves showing the results obtained with filters whose thicknesses ranged from 0 to .73 mm. are shown in figure 3.

Fig. 3.



Curve A. No aluminium.

Curve E. 0.21 mm. of aluminium.

B. 0.0140 mm. of aluminium.

F. 0.36 " " "

C. 0.0305 " " "

G. 0.73 " " "

D. 0.0446 " " "

Curves for thicknesses greater than .73 mm. are not given, as they differed inappreciably from each other. Thus, whereas the curves with the thinner aluminium screens

* Hahn and Meitner, *Phys. Zeitschr.* x. pp. 697-703 (1909).

started from different initial values, the curves with .73 mm. and greater thicknesses all rose from 10 per cent. of the maximum obtained after 32 minutes. It was therefore evident that at the end of the recoil there was present on the plate a substance emitting β rays whose coefficient of absorption was the same as that of the hard rays from RaC. Hence, either RaB gives hard rays whose coefficient is the same as that of the hard rays from RaC, or else the initial activity is due to RaC mechanically carried over with the RaB during recoil*. The latter explanation seemed, however, unlikely, as the curve (fig. 3) taken with no screen, so that the ionization was mostly due to α rays, starts more nearly from zero than any of the β -ray curves; moreover, similar results were obtained in experiments made with widely different quantities and concentrations of RaA. The possibility of explaining the observed initial activity by contamination with RaC mechanically carried over during the recoil is, however, rendered still more unlikely by experiments made with γ rays†.

The curves given in figure 3 can be used to find the ratio of the ionization produced by the β rays of RaB and RaC, in equilibrium, when measured through different thicknesses of aluminium. From the data so obtained the absorption of the β rays of RaB by aluminium can be deduced if the absorption curve for the β rays from RaC₁ is known. The calculation is carried out as follows.

Let the total ionization in the testing-vessel after 32.8 minutes be taken as a and the ionization after any time, say 2, 4, or 6 minutes, be represented by b . Now the ionization at any time is made up partly of the radiation from RaB and partly by that from RaC. Consider, first, the state of affairs after 32.8 minutes and let B be the ionization due to the RaC formed from it at the time considered. Then we have the equation

$$B + C + \epsilon C = a, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where ϵ is a small fraction and ϵC represents the quantity of RaC due to the RaC produced during the time of recoil, which was never infinitely short and varied in different experiments from 5 seconds to 25 seconds. The quantity could easily be calculated for any given experiment.

Consider now the state of affairs at some fixed time after the end of the recoil, say 6 minutes. The quantity of RaB

* See Makower and Russ, *Phil. Mag.* January 1910.

† Moseley and Makower, *infra*, p. 302.

present is greater than after 32.8 minutes in a known ratio and is, for the case of six minutes considered, about double. The quantity of RaC formed will, on the other hand, be less than after 32.8 minutes, but also in a ratio calculable from equation (1). Let B_t and C_t be the ionization due to the RaB and RaC present after a time t reckoned from the time at which the recoil was concluded. Then, since $B_t = \alpha B$ and $C_t = \beta C$, we have that

$$\alpha B + \beta C + \zeta C = b, \quad (4)$$

where b is a quantity to be determined from the curve and the term ζC is introduced for the same reason as the term ϵC in equation (3). From equations (3) and (4) B and C can be found. Now to get the absorption curve for the rays from RaB it is necessary to determine the ratio of B for each thickness of aluminium to the value of B obtained without any screen. Let the latter quantity be represented by B_0 and let C_0 be the ionization produced by RaC in equilibrium with RaB under the same conditions. Then the required ratio B/B_0 is given by the equation

$$\frac{B}{B_0} = \frac{B}{C} \cdot \frac{C_0}{B_0} \cdot \frac{C}{C_0} \cdot (5)$$

Now all the quantities on the right-hand side of the equation can be obtained from the curves given in figure 3 except the ratio C/C_0 , which has to be determined by a separate experiment on the absorption of the radiation from RaC by aluminium.

To determine the ratio of C/C_0 for different thicknesses, a nickel plate was rendered active with pure RaC by the method of von Lerch and a thin aluminium plate then rubbed on the nickel surface so as to detach some of the activity. This was done in order to have an aluminium plate of the same thickness as the absorbing plate behind the RaC, and thus to eliminate errors due to secondary radiation*. The aluminium plate was then placed in the same position with regard to the electroscope as the plates previously used in the experiments with RaB. Foils of aluminium of different thicknesses were then interposed between the active plate and the electroscope and the ionization produced measured in the usual manner. A plate of aluminium of the same thickness as the absorbing foil was in every case placed behind the active plate. After making due allowance for the decay of the RaC between successive measurements, a curve could be

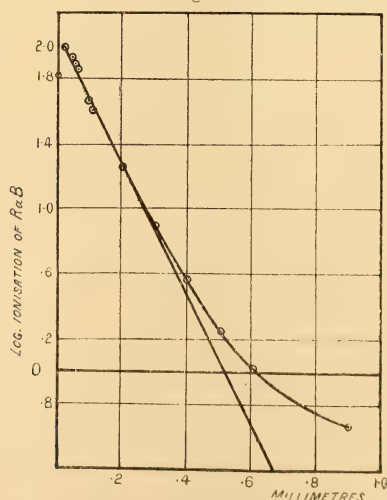
* Kovarik, Phil. Mag. Nov. 1910.

obtained giving the relation between the ionization produced in the electroscope and the absorbing layer of aluminium. From this curve the values of C/C_0 given in Table I. were found. Columns 1, 2, and 3 contain all the data necessary

TABLE I.

Thickness of aluminium in millimetres.	$\frac{B}{C}$	Absorption of RaC. $\frac{C}{C_0}$	Absorption of Radium B. $\frac{B}{B_{0.140}}$
0	0.0102	1.00	0.81
0.0140	0.0343	0.35	1.00
0.0305	0.2075	0.050	0.86
0.05	1.30	0.0073	0.789
0.06	1.24	0.0070	0.721
0.09	0.92	0.0062	0.474
0.1	0.85	0.00595	0.420
0.2	0.46	0.00465	0.177
0.3	0.25	0.00375	0.078
0.4	0.15	0.00305	0.038
0.5	0.09	0.0024	0.0180
0.6	0.06	0.0021	0.0104
0.9	0.045	0.00125	0.0047
1.3	0.045	0.00075	0.0028

Fig. 4.



for calculating the absorption of the β rays from RaB by aluminium and the absorption produced by different thicknesses of aluminium is shown in column 4. In figure 4 the

results are shown graphically by plotting the logarithm of the activities as ordinates against the thickness of the absorbing layers as abscissæ. It will be noticed that the point for 0 mm. of aluminium is much too low, no doubt on account of the smallness of the ionization due to RaB compared with that due to RaC in these circumstances. In this case the corrections to be introduced in calculating the ionization due to RaB alone are so great that accurate determinations become impossible. On this account all the values in the fourth column of Table I. are referred to the ionization produced through 0.0140 mm. of aluminium, which is taken as 100 instead of referring to thickness 0 mm.

If we consider the relative ionizations of RaB and RaC in equilibrium when measured without any screen we see that the amount contributed by RaB lies between 1 and 2 per cent. of that due to RaC. Now since under these conditions the ionization produced by RaC is mostly due to α rays, whereas that produced by the RaB is due to β rays, the relative contributions of the two products to the total ionization is about that to be expected. It will be seen that as the thickness of the absorbing filter is increased the proportion of the total ionization due to RaB increases to the value 1.33 for a thickness of 0.044 mm. of aluminium, which just suffices to cut out all the α radiation; it then falls off again as the absorbing layer increases on account of the great absorption suffered by the β rays from RaB compared with that suffered by the RaC rays. After adding about .7 mm. aluminium to cut out all the soft rays from RaB, the ratio of the ionization produced by RaB to that produced by RaC attains the constant value 0.045, showing that the remaining rays from RaB have about the same coefficient of absorption as the hard rays from RaC. It thus appears that whereas the greater part of the β radiation from RaB is soft, there is a small quantity of hard radiation which will be seen from the fourth column of Table I. to amount to rather more than 1 per cent. of the total radiation from RaB. The coefficient of absorption of these hard rays is the same as that of the hard rays from RaC, which is 13 cm.^{-1} . The coefficient of absorption of the soft rays will be seen from figure 4 to be 91 cm.^{-1} , a value which is greater than the values 80 cm.^{-1} found by Schmidt and 75 cm.^{-1} found by Kovarik. Thus the absorption coefficient obtained by us does not agree very closely with those previously obtained, and the difference is no doubt in part due to the fact that the experimental arrangement was somewhat different from those employed by Schmidt or Kovarik; but

at the same time it should be remembered that the possible errors made in deducing the coefficient from the observations are relatively great. Having regard to these two facts the agreement between the different values is perhaps as close as can be expected.

There is, however, one point of difference between our results and those of Schmidt which is of importance, for our experiments give no indication of any very soft β rays of coefficient 890 cm.^{-1} . According to Schmidt, RaB emits such rays in quantity sufficient to produce an ionization whose magnitude is about 12 per cent. of that produced by the α rays emitted by the RaC in equilibrium with it. This radiation should have been detected in our experiments if it existed; for when measuring without any aluminium screen, the rise curve should have risen from about 25 per cent. of the maximum instead of from 3 per cent. as shown in figure 3. The cause of the difference between our results and those of Schmidt is being investigated by one of us.

It should also be pointed out that Schmidt finds for the ratio of the hard rays from RaB to those from RaC the value 10 per cent., whereas we find only about 4.5 per cent., since the curves (fig. 3) for thicknesses greater than .7 mm. rise from about 10 per cent. of the maximum. The smallness of the ratio of the hard β radiation compared with that of RaC is very striking and involves interesting possibilities, but it would be premature to discuss these on the available experimental evidence.

Summary.

(1) The α rays as well as the greater part of the β rays from RaC belong to RaC₁.

(2) The ionization of the β rays from RaC₂ compared with that of the rays from RaC₁ is so small that it could not be detected in these experiments. This confirms the view that RaC₂ is not in the direct radioactive series but is formed as a side product.

(3) The β rays from RaB fall into two groups whose coefficients of absorption are respectively 13 cm.^{-1} and 91 cm.^{-1} . The ionization produced by the former amounts to only about $1\frac{1}{2}$ per cent. of the whole ionization due to RaB.

(4) No evidence could be found of the existence of rays from RaB whose coefficient is 890 cm.^{-1} .

Our thanks are due to Professor Rutherford for supplying us with the necessary emanation and for the interest which he has taken in the progress of the experiments.

XXVI. γ Radiation from Radium B. By H. G. J. MOSELEY, B.A., and W. MAKOWER, M.A., D.Sc.*

THE existence of a small amount of radiation from radium B, of the same penetrating power as the hard β rays from radium C, has been demonstrated by H. W. Schmidt† and confirmed by Fajans and Makower‡. It seemed, therefore, probable that radium B would emit a small amount of hard γ radiation of the same penetration as that from radium C. This was, however, found not to be the case; but the investigation undertaken to detect these rays has demonstrated the existence of soft γ rays from radium B which have hitherto escaped detection. Although the complete study of this radiation has not yet been made, the experiments so far carried out show the amount which the new radiation contributes to the total γ -ray activity of the active deposit of radium. It is also possible to deduce the absorption coefficient of the radiation by lead, though not with great accuracy since the number of experiments carried out was small.

The method of investigation adopted was the same as that used by Fajans and Makower in studying the β rays from radium B, except that the measurements were all made through sufficient lead to absorb all the β rays both from radium B and from radium C. Thus pure radium B was prepared by recoil from radium A and the rise of the γ radiation was measured through different thicknesses of lead. The duration of the recoil was in some cases 30 seconds and in others 90 seconds. If, as has hitherto been supposed, all the γ radiation from the active deposit of radium is due to radium C, the activity should at first be nothing and rise to a maximum after 33 minutes and then fall off with time. In practice, however, it is impossible to obtain pure radium B by the method of recoil, since in order to obtain sufficient activity, it is necessary to prolong the recoil for a finite time. The amount of radium C formed during the recoil can be calculated and the effect produced on the results allowed for; this has been done throughout in calculating the theoretical curves. The curves in fig. 1 have been calculated for the case in which the recoil lasted 30 seconds—curve A on the assumption that the activity is due wholly to the γ rays from radium C, and curve B on the assumption that γ rays from radium B also contribute to the activity. In curve B the

* Communicated by Prof. E. Rutherford, F.R.S.

† H. W. Schmidt, *Annalen der Physik*, xxi. (1906).

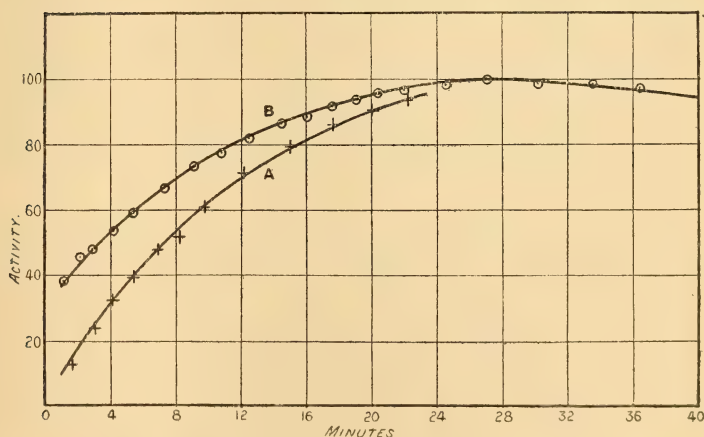
‡ Fajans and Makower, *suprà*, p. 292.

ratio of the ionizations produced in the measuring-vessel by the disintegration of an atom of radium B and radium C is taken as 14.5:100. The curves have been drawn to an arbitrary scale, so that the maximum activity is 100, and the times are reckoned from the end of the recoil. The points marked with circles in fig. 1 represent the results obtained when the surface rendered active with radium B was placed near an ordinary γ -ray electroscope such as is in general use in this laboratory. These electroscopes, which are made by Mr. C. W. Cook at the University Works, Manchester, consist of an aluminium case 2 mm. thick lined with lead 3 mm. thick. The deposit of radium B was obtained inside a glass tube 1 mm thick.

From the agreement between curve B and the experimental points it appears that the assumptions made in drawing the curve suit the experimental conditions. Stated somewhat differently, when radium B and radium C are in equilibrium, radium B contributes $\frac{14.5}{1.145} = 12.7$ per cent. of the total ionization.

The points marked with crosses in fig. 1 represent the

Fig. 1.

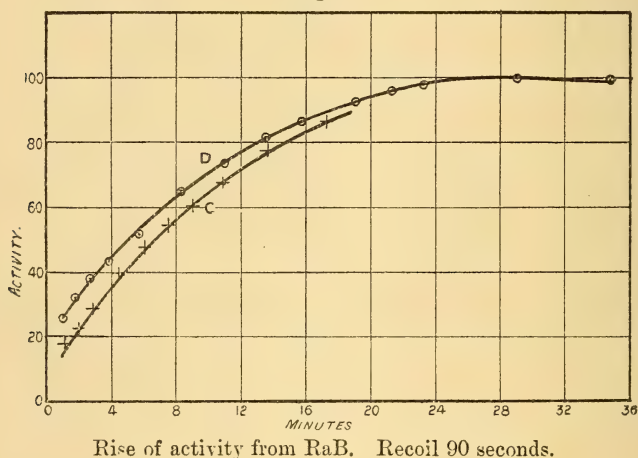


Rise of activity from RaB. Recoil 30 seconds.

results obtained with an additional 1.175 cm. of lead interposed in the path of the rays. The points lie on curve A and show that in this case all the radiation is due to radium C.

Fig. 2 shows the theoretical curves for a recoil lasting 90 seconds. Curve C represents the case in which all the

Fig. 2.



radiation is due to radium C; in curve D the ratio of the ionizations by an atom of radium B and of radium C is taken as 6 : 100. The points marked by circles were obtained through 2.95 mm. of lead in addition to the glass and the walls of the electroscope. The points marked with crosses were taken through the same screens as used in obtaining the points on curve A, fig. 1. These results show that radium B emits rays which are capable of penetrating several millimetres of lead, but which are almost completely absorbed by 1.5 cm.

The experiments so far described were entirely independent of each other, so that the possibility remained that the differences in the curves were accidental and due to contamination with radium C of the surface upon which the radium B was collected. In order to make sure that this explanation was incorrect, an experiment was made in which the same active plate produced ionization in the electroscope alternately through the electroscope walls and through an extra 1.2 cm. of lead. The curves so obtained were in substantial agreement with those given in fig. 1, showing that the initial ionization was really due to radium B.

In order to extend the investigation to smaller thicknesses of lead, a new electroscope had to be constructed. For this purpose an electroscope of dimensions 20 cm. cube was made with 5 sides of lead 1 mm. thick, the sixth side being closed

by a thin plate of aluminium. The surface coated with radium B, which in this case was entirely uncovered, was placed in front of the aluminium plate. Two experiments were made in which the absorbing sheets of lead were 0.97 mm. and 1.72 mm. respectively. The results indicated that for radium B and radium C in equilibrium 16.7 per cent. of the ionization is due to radium B when measuring through 0.97 mm. of lead, and 12.3 per cent. through 1.72 mm. of lead.

It is evident that the radiation from radium B is much softer than that from radium C. An idea of the coefficient of absorption of the radiation by lead can be formed if it is known how the radiation emitted by radium B and radium C in equilibrium is absorbed. This absorption was found for the greater thicknesses of lead by using as the source of radiation radium emanation enclosed in a glass tube. For the smaller thicknesses of lead this source could not be used on account of the necessity of doing away with the glass envelope. In this case, therefore, a plate was made active with radium B and measurements taken in the neighbourhood of 33 minutes after preparation, at which time the radium B and radium C produced from it were in equilibrium. The absorption coefficient of the γ rays from radium B can then be calculated from the observations.

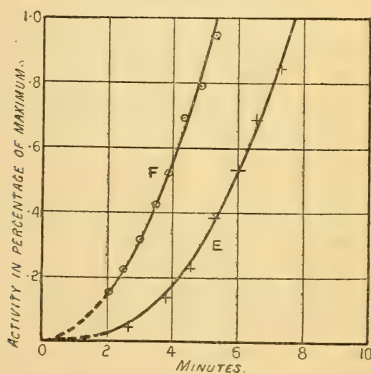
It was found that the coefficient of absorption λ is 4 cm.^{-1} between 3 mm. and 6 mm. of lead and is 6 cm.^{-1} between 0.97 and 1.72 mm. of lead. It will therefore be seen that the γ rays from radium B are much softer than the penetrating radiation from radium C given by F. & W. M. Soddy and Russell* as having an absorption coefficient 0.5 cm.^{-1} over a wide range.

The method described above, though suitable for testing whether there is any considerable γ radiation from radium B, is not the best possible for seeing whether there is a small amount of hard γ radiation emitted by this product; for the quantity of radium B obtainable by the method of recoil is not great, so that a small amount of hard radiation might escape detection. A better method of testing the point is to observe the rise of activity of radium emanation, which has been completely freed from the active deposit associated with it. In such an experiment γ rays from radium B make themselves easily noticeable. This would appear to be the best method of obtaining precise values for the absorption of the soft rays; but on account of the doubtful significance of such measurements, this investigation has not been pursued.

* *Phil. Mag.* May 1910.

In order to prepare pure radium emanation in sufficient quantity to carry out the desired experiment, about 30 millicuries of emanation mixed with air were exposed at atmospheric pressure to a strong electric field for 3 hours, to render it as free from active deposit as possible. The emanation was then quickly forced through a plug of glass wool into a glass tube which was sealed off in a blow-pipe. The tube was placed in position near the electroscope and measurements begun. The activity was at first so small as to be incapable of detection, and then rapidly rose as measurements were continued till the activity became too great for further observations. The tube was then moved further from the electroscope and measurements continued till the emanation had attained its maximum activity. In order to deduce a complete curve showing the rise of activity of the emanation, a careful comparison was made of the ionizations produced in the two positions by the active deposit left in the tube after removing the emanation and waiting for the activity to decay to a convenient amount. The results obtained for the first few minutes through 2.3 cm. of lead are marked with crosses in fig. 3, in which the activities are expressed in percentages of the maximum reached after about

Fig. 3.



Rise of activity from pure emanation.

four hours. The fact that the activity was too small to measure at the beginning of the experiment shows that the emanation contained not more than about 0.01 per cent. of the equilibrium amount of active deposit. This fact is somewhat remarkable. It will further be noticed that the experimental results lie closely on curve E, fig. 3. This

curve has been drawn on the assumption that all the rays come from radium C and none from radium B. The activity is proportional to N , the number of atoms of radium C disintegrating per second which can be calculated from the following equation :

$$N = \lambda_2 \lambda_3 \lambda_4 \sum_{\lambda=1,2,3,4} \frac{e^{-\lambda_1 t}}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)(\lambda_4 - \lambda_1)}, \quad \dots \quad (1)$$

where the number of atoms of emanation disintegrating per second at the beginning is taken as unity and $\lambda_1, \lambda_2, \lambda_3$, and λ_4 are the decay constants of the emanation, radium A, radium B, and radium C respectively. N reaches a maximum value 0.9721 after 258 minutes. In drawing the curves in fig. 3, this value has been taken as 100.

The curve E, fig. 3, has been plotted only for the first few minutes, but the agreement between theory and experiment is so satisfactory for the whole time during which the activity of the emanation rises that the values of the activity at different times can be taken from column II. of the Table given in the appendix. In the third column of this table are given the numbers calculated on the assumption that 11.5 per cent. of the ionization is due to radium B and the rest to radium C, when radium B and radium C are in radioactive equilibrium. The curve obtained on this assumption is plotted in fig. 3, curve F. The experimental points obtained when measuring through the walls of the ordinary γ -ray electroscope mentioned above agreed well with this assumption, and the points obtained in this case are marked in fig. 3 with circles. This curve is similar to that given by Rutherford * in his Bakerian Lecture, p. 199, which was obtained from measurements taken through a considerable thickness of matter. The difference from the curve, calculated on the assumption that radium B is rayless, is therefore no doubt due to the emission of γ rays by radium B and not to the soft β radiation emitted by it as has sometimes been supposed.

The agreement between theory and experiment when measuring through 2.3 cm. of lead indicates that the amount of hard γ radiation from radium B compared with that from radium C is extremely small. There can be no doubt that if such radiation exists the ionization produced by it through 2.3 cm. of lead does not amount to 1 per cent. of that produced by radium C, if the decay constants assumed are correct.

* Rutherford, Phil. Trans. A. 204 (1904).

Finally, fig. 3, curve E gives interesting information on the question of the amount of radium C_2 produced from radium C_1 . It has been suggested by Fajans* that radium C_2 is produced only in small quantity from radium C_1 , so that if γ rays as well as β rays are emitted by this product, they would not be likely to contribute more than a small percentage of the total γ radiation from the active deposit. The agreement between theory and experiment shown in fig. 3, curve E, for the case of 2.3 cm. of lead, proves that radium C_2 cannot emit any considerable amount of hard γ radiation. If radium C_2 contributed 10 per cent. of the total radiation, there would have been obtained a detectable deviation from curve E, fig. 3. The activities measured for the first few minutes were so small that the small differences between theory and experiment may be disregarded. The results are therefore in agreement with the result obtained by Fajans that radium C_2 is formed from radium C_1 as a side product, and is not in the direct radioactive series.

Summary.

(1) γ rays of absorption coefficient about 4 cm.^{-1} for lead between the thicknesses 3 mm. and 5.94 mm. and about 6 cm.^{-1} between 0.97 mm. and 1.72 mm. are emitted by radium B. These rays contribute about 12 per cent. to the total ionization produced by the active deposit measured through 3 mm. of lead and not more than 1 per cent. through 2.3 cm. of lead. Radium B appears, therefore, to give no hard γ radiation.

(2) Radium C_2 , if it emits γ rays at all, gives an amount too small to be detected by the method used.

Our best thanks are due to Professor Rutherford for his interest in this research, and for lending us some unpublished observations for comparison with our results.

APPENDIX.

Table for calculating the rise and fall of activity from Pure Radium Emanation under different conditions.

Column II. gives the number of atoms of radium C present at different times in a closed vessel after admitting pure emanation. The maximum value, which is taken as unity, occurs after 258 minutes. The numbers are calculated from the equation :

$$N_{II} = \frac{\lambda_2 \lambda_3 \lambda_4}{.97213} \sum_{\lambda=1,2,3,4} \frac{e^{-\lambda_1 t}}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)(\lambda_4 - \lambda_1)}.$$

* Fajans, *Physik. Zeitschr.* xii. p. 369 (1911).

This equation represents the variation of activity as measured through 2·3 cms. of lead.

I. Minutes.	II. Calculated rise of Radium C from pure emanation.	III. Calculated rise of ionization by γ rays for ex- perimental case.	IV. Calculated fall of Radium C after removal from emanation.	V. Calculated fall of ionization by γ rays for experi- mental case.
0.....	0·0000	0·000	1·0000	1·000
2.....	·000252	·00143	·9995	·998
3.....	·000801	·00323	·9989	·997
4.....	·001770	·00570	·9978	·994
5.....	·003239	·00885	·9963	·991
6.....	·005244	·0126	·9942	·987
8.....	·01097	·0221	·9884	·978
10.....	·01899	·0338	·9805	·966
12.....	·02925		·9703	
14.....	·04154		·9582	
15.....		·0719		·929
17.....	·06343		·9368	
20.....	·08876	·118	·9120	·884
25.....	·1368	·170	·8650	·833
30.....	·1897	·225	·8134	·779
40.....	·3015	·338	·7046	·669
50.....	·4118	·446	·5985	·566
60.....	·5125	·543	·4987	·469
70.....	·6021	·629	·4112	·385
90.....	·7440	·763	·2719	·253
120.....	·8775	·888	·1396	·129
150.....	·9468	·952	·06913	·0639
180.....	·9800	·982	·03347	·0308
240.....	·9994	1·00	·00752	·00691
258.....	1·000	1·00		
270.....			·00352	

Column IV. gives the number of atoms of radium C left in a vessel at different times after completely removing the emanation which has been confined in it for a long time. The numbers are calculated from the equation

$$N_{IV} = e^{-\lambda_1 t} - \frac{\lambda_2 \lambda_3 \lambda_4}{1 \cdot 00891} \sum_{\lambda=1,2,3,4} \frac{e^{-\lambda t}}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)(\lambda_4 - \lambda_1)}.$$

This equation gives the fall of activity measured through 2·3 cm. of lead.

Column III. gives the ionization at different times after the introduction of pure emanation on the assumption that

when in radioactive equilibrium radium B contributes 11.5 per cent. of the ionization and RaC 88.5 per cent.

$$N_{III} = \frac{.115}{.97213} \lambda_2 \lambda_3 \sum_{\lambda=1,2,3} \frac{e^{-\lambda_1 t}}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)} \\ + \frac{.885}{.97213} \lambda_2 \lambda_3 \lambda_4 \sum_{\lambda=1,2,3,4} \frac{e^{-\lambda_1 t}}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)(\lambda_4 - \lambda_1)}.$$

This equation gives the ionization as measured in a Cook γ -ray electroscope.

Column V. gives the fall of ionization, reckoned on the same assumption as used in calculating column III., after completely removing from a vessel emanation which had been confined in it for a long time.

$$N_V = e^{-\lambda_1 t} - \frac{.115}{1.0085} \lambda_2 \lambda_3 \sum_{\lambda=1,2,3} \frac{e^{-\lambda_1 t}}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)} \\ - \frac{.885}{1.0085} \lambda_2 \lambda_3 \lambda_4 \sum_{\lambda=1,2,3,4} \frac{e^{-\lambda_1 t}}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)(\lambda_4 - \lambda_1)}.$$

This gives the rate of decay of radium active deposit, completely separated from emanation, as measured with a Cook electroscope. The values of λ assumed in these calculations are the following expressed in (second) $^{-1}$:

$$\lambda_1 = 2.08 \times 10^{-6}, \lambda_2 = 3.85 \times 10^{-3}, \lambda_3 = 4.33 \times 10^{-4}, \lambda_4 = 5.93 \times 10^{-4}.$$

XXVII. *Diffraction Gratings with Controlled Groove Form and Abnormal Distribution of Intensity.* By R. W. WOOD, *Professor of Experimental Physics, Johns Hopkins University* *.

IN the Philosophical Magazine for September 1902 I published an account of a diffraction grating, ruled on speculum metal, which exhibited a most remarkable distribution of intensity of the energy in some of the spectra. The continuous spectrum of a white source was interrupted by bright and dark bands sometimes not over 20 or 30 Ångström units in width, which appeared most distinct

* Communicated by the Author.

when the direction of the electric vector was perpendicular to the direction of the groove, and vanished when these directions were parallel.

In the present paper I shall describe a still more remarkable grating which shows a bright *line* in the continuous spectrum of a white source, which by actual measurement is only 3 Ångström units in width, *i. e.* of a width equal to one half of the distance between the D lines. As the angle of incidence is varied the position of the bright line in the spectrum changes, and, what is of especial interest, its wave-length corresponds exactly to the wave-length which is just passing off from the grating at grazing emergence in the 4th order spectrum. This is in agreement with the surmise expressed by Lord Rayleigh (Phil. Mag. July 1907), that abnormalities are to be expected at such angles of incidence that spectra of higher orders are just passing off. The bright line in question appears in the first order spectrum on the opposite side from that on which the grating concentrates light, and is about as bright as the continuous spectrum upon which it appears projected, so that the brilliancy at the point in question is about double that of the rest of the spectrum. In viewing the spectrum of the arc, the bright line resembles the bright lines which sometimes flash out upon the continuous spectrum of the crater.

As I showed in my paper upon the echelette grating (this Journal, Oct. 1910), if a grating is ruled upon a polished surface of a soft pure metal instead of on a hard alloy such as speculum metal, the form of the groove can be made to conform more perfectly to that of the ruling point, which moreover does not wear away rapidly as is the case when the ruling is done on a hard alloy. In the case of the echelette gratings I used a surface of gold-plated copper, which gave such excellent results that I immediately tried to find a surface suitable for optical gratings. A very thin coating of silver was deposited upon a plate of polished speculum metal by electrolysis, and was then very carefully polished. This was found to serve admirably, and a trial grating, with 14,438 lines to the inch, was ruled with the old Rowland machine, which showed a very dark central image and a very bright first order spectrum. Spectra were also obtained on plates prepared in this way which yielded spectra in which certain colours were wholly absent, the dark bands reminding one forcibly of the dark bands observed with the curious grating described in 1902, except that they were much wider.

Dr. Anderson, who has had charge of the dividing engines,

informed me that he had found a diamond point which ruled gratings showing anomalies similar to those which I described in the earlier paper, and he has ruled me a number of gratings upon a thin silver surface deposited upon a speculum plate. The lines are ruled at the rate of 10,000 to the inch on the so-called 20,000 machine. The first order spectrum on one side is very bright, while that on the other is quite faint, and it is in this faint spectrum that the abnormalities are found. This grating appears to be of such good quality that it seems probable that excellent optical gratings of very large size can be made in this way. We can choose our metal according to the region in which we wish to work. Gold, for example, would be far better than speculum metal for the region between 5500 and 8000, for gold reflects 90 per cent. in the red, while speculum metal reflects only 65 per cent., a matter of some importance for example in the study of the resonance spectra of iodine, which are not very bright and fall exactly within this region.

Gratings made in this way would have to be handled very carefully however, for I have found that the lightest possible rubbing with soft chamois skin alters the distribution of the light in the spectra in a most remarkable manner. It is possible in this way to raise the intensity of the faint first order spectrum four- or fivefold and cause the dark bands to disappear entirely. It is quite interesting that the groove form can be thus "figured" after the grating is ruled, though I doubt whether the efficiency of a grating could ever be improved in this way, since the tendency seems to be always to give a more uniform distribution of light among the spectra, which is precisely what we do not want. This "figuring" of the groove has, however proved of value in the study of the bright and dark bands as they can be developed in intensity in this way, and caused to change their position in the spectrum.

While the present study has not completely solved the question of the cause of the remarkable anomalies, many additional experimental data have been obtained, and it is possible that the results may point to the modifications necessary to make Lord Rayleigh's theory cover the ground.

I shall now describe in detail the observations made with one of the gratings. The groove form is probably quite similar to that used in the case of the echelette gratings, one side very steep, the other making only a small angle with the original surface. This is similar to that of the grating described in 1902, from which I made a cast at the time

with celluloid deeply stained with an aniline dye, which was sectioned with a microtome and examined under the microscope. The grating was mounted on the table of a large Fuess spectrometer so arranged that the table turned with the graduated circle. At normal incidence it showed a black band in the red about 30 Ångström units in width, the centre of which was at 6560, and a bright line 3 Ångström units wide at 6400.

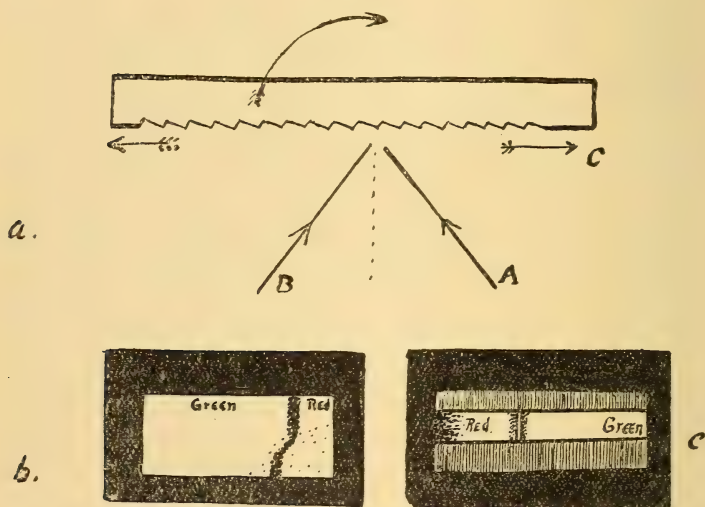
The telescope and collimator were not used, the spectrum being viewed by the eye directly. The source of light was a Nernst filament situated at a distance of about 3 metres from the grating, with a very brilliant neon tube immediately behind it. A Nicol prism was mounted in front of the lamp, for the bands appeared at their best with polarized light (electric vector perpendicular to the grooves). Behind the neon tube an arc lamp was mounted for producing the very intense illumination necessary for the experimental determination of the wave-length of the light passing off from the grating at grazing emergence. On viewing the spectrum in the grating, the dark band or the bright line could be brought into coincidence with some one of the numerous bright neon lines, by changing the angle of incidence.

As a check on this method of determining the position of the bands the arc was lighted, and a Schmidt and Haensch pocket-spectroscope, provided with an illuminated scale of wave-lengths, was directed at the spectrum seen in the grating. The dark band then appeared in the spectrum seen in the small spectroscope, and its wave-length could be read off at once. The width of the bright band was determined with the large spectrometer with fixed telescope and collimator of 2.5 metres focus, by comparison with the D lines.

Considering the grating mounted as in fig. 1 *a*, the faint first order spectrum in which the abnormalities are seen is viewed in the direction A. The first order spectrum on the other side (direction B) is extremely bright, being favoured by the broad, gently sloping sides of the groove. The spectra passing off at grazing emergence are very bright in the direction C and very faint in the direction D, as is to be expected, for the steep, narrow sides of the groove favour the direction C. The circle of the spectrometer was set at zero, and the grating turned on the table until the incidence was normal, as determined by reflecting the image of the ruled spot back to the arc.

The spectrum seen in the direction A exhibited a dark band in the red and a very faint narrow bright band in the orange. Previous experiments with another grating having

Fig. 1.



shown that lightly wiping the surface modified the appearance of the bands, an attempt was made to better them in the case of this grating. A very light rubbing with a powder-puff made of swan's down increased the blackness of the dark band and increased the narrowness and intensity of the bright band, which presently with a little further rubbing became a line. The lower corner of the grating was now rubbed lightly with chamois skin. This operation obliterated all trace of the bright line, and caused the dark band to shift into the yellow-green region. If the spectrum was made to cover the entire surface of the grating by bringing the source of light nearer, the dark band in the red was seen to pass gradually into the green region, the band appearing curved, as shown in fig. 1 *b*. In this figure the lower right-hand corner of the ruled surface has been rubbed with chamois skin.

The relations between the positions of the bright line and dark band and the angles of incidence were now determined. The circle was turned so as to rotate the grating in a clockwise direction (fig. 1 *a*) through an angle of 11° . The dark band moved from the red down into the green, preceded by the bright line which remained distinct up to a rotation of

9° but disappeared at 11°. Its disappearance may have been due to its having passed into the blue region, in which the eye cannot see as sharply as in the more luminous regions. In the following table are given the positions of the bands for various angles of incidence. The wave-lengths passing off at grazing emergence in the direction C are given in the fourth column.

Incidence Angle.	Dark band.	Bright line.	Passing off.
11°	5500		5150
9°	5650	5340	5340
6° 20'	5900	5650	5650
4° 55'	6000	5800	5800
3° 55'	6100	5940	5940
2° 50'	6200	6030	6030
1° 30'	6400	6200	6200
0	6560	6350	6350
1° 10'	6650	6520	6520
1° 50'	6600	6600	6600
2° 40'	6720	6720	

As will be seen from this table, the wave-length of the bright line agrees in each case with that of the light which is passing off the grating in the fourth order. As the grating is turned in a clockwise direction the two bands move towards the region of greater wave-lengths, the bright line a little more rapidly, until at an angle of 1° 50' on the other side of normal incidence the bright line moves into the centre of the dark band, appearing as shown in fig. 1 c.

This entrance of the bright band into the dark one is very interesting, and should be a valuable clue to the origin of the bands. The wave-length of the dark bands, for in the case of some of the gratings several dark bands appear, bears no relation to that of any of the colours which are passing off the grating at grazing emergence, though in general they seem to correspond to wave-lengths diffracted at angles a little greater than grazing emergence; in other words, to result from disturbances which come from the steep side of the groove and are reflected against the opposite side.

It was found that certain anomalies appear when the direction of the electric vector is parallel to the groove. For example, if we hold the nicol in front of the eye and allow unpolarized light to fall upon the grating, the dark band appears in the orange (incid. angle 5°) when the short diagonal of the nicol is horizontal, *i. e.* when the electric vector is perpendicular to the groove. If now we rotate

the nicol through a right angle the entire red end of the spectrum above the dark band disappears, the portion of the spectrum vanishing in this case being at least five or six times the width of the dark band.

A study was also made of the polarization of all of the spectra and the central image. Though I doubt if these data will prove of material assistance in the development of a theory accounting for the bright and dark bands, I will include them for the sake of making the study as complete as possible.

The grating was set at normal incidence which brought the dark band to wave-length 656. The incident light was unpolarized, and the spectra examined through a nicol. In the first order spectrum all of the light on the red side of the dark band was polarized $\perp$, the rest of the spectrum showed an excess of $=$ polarization. In the second and third orders on the same side, the red end was nearly completely polarized $=$, the remainder showed an excess of $\perp$ polarization. The fourth order was completely polarized $=$.

On the other side of the central image the very bright first order spectrum showed little or no trace of polarization. In the second order the red end was completely polarized $\perp$. Third order no polarization, and fourth order all $\perp$. The central image, examined with a spectroscope, showed a dark band at 650, and all longer waves were found to be polarized $\perp$ as in the faint first order spectrum. The $\perp$ and $=$ signs referred to above denote the direction of the electric vector with respect to the direction of the groove.

It is a matter of some importance to ascertain what becomes of the light which is absent in the spectrum. If one spectrum shows a dark band we should expect some other spectrum to show a bright band at the same point. This, however, is not the case, and we may infer from this that the absent energy is distributed amongst the other spectra, the amount received by each being too small to be noticeable.

It appears to me that the present paper contains sufficient experimental data to thoroughly test any theory which may be developed to account for these remarkable anomalies. It seems evident that they are to be referred to the action of the sharp ridges and not to the bottoms of the grooves, as they are profoundly modified by the lightest possible rubbing of the grating with soft chamois skin.

The extraordinary narrowness of the bright line (3 A.E.) undoubtedly requires the co-operation of a large number of lines, and it is to be noticed that its wave-length agrees

exactly with that of the light which is passing off the grating on the side towards which light is reflected from the steep sides of the grooves. It is worthy of remark that the tops of the ridges will be illuminated by diffracted light of the right wave-length, though this circumstance alone is not sufficient to account for the narrowness of the bright line. The shift of the dark band towards the region of shorter wave-lengths produced by lightly rubbing the surface of the grating should prove an important clue, as well as the unequal rate of advance of the bright line and dark band along the spectrum as the grating is rotated.

If any further experiments are required to test any theory which may be developed, they can be made without difficulty.

XXVIII. *Ionization in Gaseous Mixtures by Röntgen Radiation.* By Prof. C. G. BARKLA, M.A., D.Sc., and L. SIMONS, B.Sc., University of London, King's College*.

THE intimate connexion between the ionization in a gas by X-rays and the secondary radiation from the elements constituting the gas was first shown by one of the writers in a letter to 'Nature' on "Ionization by Röntgen Rays" †. It was shown that the emission of a fluorescent X-radiation from a constituent element of a gas traversed by X-rays was accompanied by a considerable ionization in the gas itself. Later papers ‡ established the generality of the connexion, and showed that a considerable portion of the increased ionization was due to the secondary corpuscular radiation. It was estimated that something of the order of one third of the total ionization was due to the corpuscular radiation; but it was pointed out that as the assumptions on which the calculation was based were only approximately true, the precise fraction could not be determined. Experiments by Bragg § showed the same thing, for though the results published indicated that about 10± per cent. of the ionization produced by X-rays was due to secondary corpuscular radiation, it is evident that the agreement between the whole ionization and that calculated as due to corpuscular radiation is quite accidental, several of the assumptions giving no more than an approximation to the truth. Even the last assumption that the absorption of air is entirely due to nitrogen and oxygen is wrong by an amount which would

* Communicated by the Authors. The expenses of this research were partially covered by a Government Grant through the Royal Society.

† 'Nature,' April 15, 1909.

‡ Phil. Mag. Aug. 1910.

§ Phil. Mag. Sept. 1910.

raise 104 per cent. to about 130 per cent. There are possibilities of much greater error, but this is one which may be easily corrected, and it shows that the conclusion from the experiment is not what at first sight it appears.

Again, in a later paper by Bragg and Porter (Proc. Roy. Soc. A. vol. lxxxv. 1911), results are given with the object of showing that all the ionization produced in oxygen by X-rays can be accounted for by the secondary corpuscular radiation. A serious error, however, completely changes the significance of the results. The mass absorption coefficient $\left(\frac{\lambda}{\rho}\right)$ for Sn X-rays in oxygen is found by experiment to be .425, and it is assumed that all of the energy so accounted for is truly absorbed in the oxygen. As a matter of fact, .2 of the .425, or nearly one half, is scattered*, and in the experiments described practically all this was lost. If, then, we accept all the experimental data given, the final comparison is no longer between 34 and 36.3, but between 34 and 68.4; in other words, only half the ionization in oxygen is accounted for.

We do not venture to use these results as an argument against the hypothesis of ionization by secondary corpuscular (electronic) radiation. We do say, however, that these experiments furnish no direct evidence in favour of it. For the present we must leave the question open, with the expression of opinion that on the whole the balance of evidence is against.

Beatty's experiments † probably give us the most exact information on the point. He concluded that fractions varying up to 75 per cent. of the total ionization in seleniuretted hydrogen were due to corpuscular radiation. But, again, these results give only the order of magnitude. A small error in his assumptions might easily change 75 per cent. into 100 per cent. Neither experiments on gases at various pressures nor in chambers of various lengths show the effect of extremely easily absorbed corpuscular radiations such as might be and in all probability are set up by very soft fluorescent X-radiations produced by the primary X-rays.

It was thought that experiments made upon the ionization produced by X-rays in certain gaseous mixtures would probably throw some light on the processes involved, for, as will be seen, we can to some extent distinguish between the direct and secondary effects, possibly even though the secondary rays be so soft as to be absorbed by the molecules in the immediate neighbourhood of the radiating atoms.

* Barkla, Phil. Mag. May 1904; May 1911.

† Proc. Roy. Soc. A. vol. lxxxv. 1911.

Apparatus.

Various pieces of apparatus were used in the following experiments to measure the ionization in gases. The ionization-chamber itself was usually cylindrical in shape. One flat end was provided with a thin aluminium window to admit the ionizing radiation; the opposite end was made of brass or lead, with an internal facing of thick aluminium, upon which the radiation fell after traversing the gas. The sides of the cylinder were also aluminium-lined. The terminal in this ionization-chamber was in some cases axial, in others circular in a plane parallel to the ends. This terminal was connected by a vertical wire passing through a brass connecting-tube with an electroscope of the type used in many previous experiments. Deflexions of the gold-leaf were, as usual, observed by means of a microscope with micrometer eyepiece, and the rate of deflexion was taken as a measure of the ionization in the vessel above, when the saturation-current was obtained.

The radiations used were the homogeneous fluorescent Röntgen radiations* emitted by elements when these were exposed to ordinary primary Röntgen radiations. Two ionization-chambers and connected electroscopes were invariably used, each receiving a beam of homogeneous Röntgen radiation from the same sheet of substance placed in the primary beam. One chamber contained air, and was used to standardize the intensity of fluorescent X-radiation from the particular substance used; while the gas in the other chamber was varied in order to study the relative ionizations in various gases.

The following experiments were performed :—

Ionization in SH_2 and SO_2 .

In experiments by one of us† on the gases sulphuretted hydrogen and sulphur dioxide, it had been found that the ionization in the former gas produced by beams of X-rays was invariably greater than the ionization in sulphur dioxide at the same temperature and pressure, whatever the penetrating power of the ionizing radiation. As the absorption in oxygen is much greater than that in hydrogen, and as it has always been found that absorption is a purely atomic phenomenon, the results suggested that the greater absorption of X-rays in SO_2 was accompanied by less ionization than that in SH_2 , indicating that ionization is not proportional to absorption, and that the process of ionization is not purely atomic, but depends on chemical combination. These conclusions had been arrived at by various experimenters.

* Phil. Mag. Sept. 1911.

† Results not yet published.

but had latterly been received with some scepticism. Indeed, the experiments had been made with little knowledge of the laws of secondary radiation. It was important that the question should be conclusively settled. To thoroughly test the relative ionizations in SH_2 and SO_2 , experiments were made by us with X-radiations varying enormously in penetrating power from that characteristic of Cr (series K) to that characteristic of Sb (series K) and many intermediate penetrating powers. Various ionization-chambers of three entirely different types were used, the lengths varying from 1 cm. to 12 cm.; the windows and ends of these were of carbon, paraffin-wax, and aluminium; the terminals were of various forms—some exposed to the X-radiation, others not exposed. Both gases SH_2 and SO_2 were prepared in different ways, in some cases containing a large quantity of aqueous vapour, in others exceedingly dry. Large variations were also made in the intensity of the radiations to which the gases were exposed until the limits of accurate measurement were reached, but no variation of relative ionization was observed; so that there appears no possibility of the saturation-current not having been reached. Only in the case of the short ionization-chamber in which the end-effects were large and unknown did accurate experiments show variations

TABLE I.

Ionizing radiation: the fluorescent X-radiation (series K) from Ag.

Length of Ionization-chamber.	Gas Ionized.	Observed Relative Ionization.	Corrected Ionization.	Relative Ionization.
3.5 cm.	Air	1.00	.7	1
	SH_2	10.6	10.7	15.3 } ratio
	SO_2	8.5	8.6	12.3 } 1.24
11.5 cm.	Air	1.17	1.09	1
	SH_2	16.4	17.0	15.6 } ratio
	SO_2	13.5	14.1	12.9 } 1.21
11.5 cm.	Air	1	.89	1
	$\text{SH}_2 + \text{O}_2$	7.5, 7.4	7.7, 7.6	8.65, 8.55 { ratio
	$\text{SO}_2 + \text{H}_2$	6.46, 6.3	6.6, 6.45	7.4, 7.25 { 1.16 1.17

NOTE.—In the first set of three experiments the air-ionization was corrected for end corpuscular radiations [from Sadler's results], and the SH_2 and SO_2 ionization corrected for absorption. The boundary corpuscular radiation effect in these was negligible. Window and end were of Al.

In the second set of three experiments a correction for corpuscular radiation from the end was not made, as it was of paraffin.

In the third set of three experiments corrections were made for corpuscular radiation from the ends when air was ionized, and for absorption in the gaseous mixtures.

greater than the possible errors of experiment in the relative ionizations produced by a given radiation. Typical results are given in Table I.

As the ionization was exceptional, it seemed advisable to directly measure the absorption of X-rays in these two gases. This was done by Mr. Collier, who found the absorption in SO_2 greater than in SH_2 by an amount about equal to the absorption in O_2 . This result showed there was no violation of absorption laws, and that impurity was not producing any appreciable effect.

Thus the ionization and absorption in these two gases are in the reverse order of magnitude. The fact would not be remarkable, however, if the secondary rays were not also accounted for. But the secondary corpuscular radiation was all absorbed in both gases with the exception of that from a very thin layer at the boundaries of the ionization-chamber. The resultant effect of this must have been exceedingly small in these two gases, and have actually entailed greater loss by the SH_2 than the SO_2 . The difference must have been inappreciable. Again, the fluorescent X-radiations emitted by S are very absorbable, and must have been more absorbed in SO_2 than in SH_2 , owing to the higher absorbing power of O_2 than H_2 . Finally, though there is the possibility of the energy of fluorescent X-radiation escaping from O_2 being greater than that from H_2 , the maximum possible difference would again be inappreciable. There seemed, therefore, little doubt of the less absorption in SH_2 being accompanied by the greater ionization. This, however, by no means proved that ionization is not an atomic phenomenon. For sulphur atoms might emit the same amount of corpuscular radiation in both gases; but whereas in SH_2 the corpuscles would be almost entirely absorbed in sulphur, in SO_2 they would be partially absorbed in sulphur and partly in oxygen. Thus the difference might be due to the greater production of ions from sulphur than from oxygen by the absorption of the same amount of energy of corpuscular radiation. This would still leave ionization a strictly atomic phenomenon.

In order to determine if ionization is truly atomic and at the same time to further test the observed absence of proportionality of ionization and absorption, experiments were made on the ionization in mixtures of SH_2 and O_2 at equal partial pressures and of SO_2 and H_2 . In these mixtures we have the same elementary constituents in the same proportion. They therefore absorb all radiations to an equal extent, and each constituent is subject to the same radiation in the two cases. The results show a decided difference

between the ionization in the two mixtures, SH_2 and O_2 being ionized to a greater extent than SO_2 and H_2 , the ratio being found to be 1.16 and 1.17 in two separate experiments (Table I.) when the Ag X-radiation (series K) was used as the ionizing agent.

These results appear to us to furnish conclusive proof that (1) ionization by X-rays is not fundamentally atomic, but depends to a certain extent on chemical combination; (2) equal absorption of X-rays and their secondary rays are accompanied by unequal ionizations.

Direct experiments on ionization and absorption certainly point to the conclusion that when a definite amount of energy of X-radiation is absorbed, and with it all known secondary radiations, the ionization accompanying this absorption depends to a certain extent on the nature of the absorbing substance. Thus, comparing the absorption of the Cu or Zn X-radiation (series K) in SH_2 and air, the ratio of the absorption coefficients for the two gases under similar conditions of temperature and pressure = 11.3, or = 11.6 allowing for scattering.

But the ratio of ionizations in the gases is 14.7.

Thus, using Cu X-radiation,

$$\frac{i_{\text{SH}_2}}{i_{\text{air}}} = 14.7. \quad \frac{(\lambda - s)_{\text{SH}_2}}{(\lambda - s)_{\text{air}}} = 11.6 *.$$

Similarly,

$$\frac{i_{\text{SO}_2}}{i_{\text{air}}} = 11.7. \quad \frac{(\lambda - s)_{\text{SO}_2}}{(\lambda - s)_{\text{air}}} = 12.7.$$

Now there is strong evidence that the fluorescent X-radiations from air are much softer than those from S (which is the important term in SH_2 and in SO_2), and that a much greater proportion of these are absorbed in air than of S X-radiations in SH_2 or SO_2 . And it may be shown that in these experiments the S X-radiation escaping from the ionization-chamber was not more than 4 or 5 per cent. of the whole fluorescent X-radiation, and therefore much less of the whole energy absorbed; consequently the energy escaping from the air must have been inappreciable. Again, practically all the corpuscular radiations were absorbed, so that unless there were excited in air by Cu X-radiation, X-radiations more penetrating than any of which we know

* $\frac{s}{\lambda}$ is the fraction of the absorption coefficient due to scattering.

(belonging to another series in fact), we may conclude that more ions were formed in SH_2 than in air for corresponding absorptions. We conclude, therefore, that about 30 per cent. more ions are formed in SH_2 than in air by the complete absorption of energy of soft X-radiation characteristic of Cu.

On the other hand, it appears that the energy required to produce an ion in SO_2 is slightly more than that required to produce an ion in air.

By similar reasoning we conclude that the energy of X-radiation absorbed during the production of an ion in ethyl bromide is considerably less than that in air, and even in SH_2 .

The relative energies absorbed during the production of equal ionizations in several gases are approximately :

Air	1.
SH_2	·79.
SO_2	1·08.
$\text{C}_2\text{H}_5\text{Br}$	·70, or less.

It should be pointed out that Langevin found for the ratio in SH_2 and air the value ·72. The other gases were not experimented upon by him. Crowther obtained differences of the same order for other gases, using heterogeneous beams of X-rays, and Kleeman showed differences of like order in the ionization, both by secondary corpuscular radiation produced by X-rays and by α rays*.

Ionization by Corpuscular Radiation.

As the ionization produced in the mixtures of $(\text{SH}_2 + \text{O}_2)$ and $(\text{SO}_2 + \text{H}_2)$ by X-rays were decidedly different, it became a matter of interest to determine whether corpuscular radiation would produce equal ionizations in these mixtures, or if the relative ionizations would be the same as found when the ionization was by X-rays.

In order to test this, a very short ionization-chamber was used so as to make the end effect large. It consisted of a flat box 8 cm. square and 1 cm. in thickness, with both faces of carbon. Thus, the window through which the rays entered and the back surface upon which these rays fell were of carbon, so that the corpuscular radiation from the two faces was small. The gases consisting of elements of higher atomic weight would on the whole lose in corpuscular radiation at the boundary. This loss is, however, of no importance here.

* From Bragg's experiments.

The ionizations of the two mixtures were determined, the silver fluorescent X-radiation (series K) being used. Both internal faces of the ionization-chamber were then covered with gold-leaf of $\cdot 00017$ gram per square centimetre—gold being used to produce an intense corpuscular radiation—and the ionizations were again determined while the same beam of X-rays was employed. As the absorption by the gold-leaf of the X-radiation used was negligible, the difference between the ionizations in the two cases was due to secondary rays from gold,—or more strictly to the difference between the rays from carbon and from gold.

Now the effective radiation so close to a gold radiator is the corpuscular radiation*. We therefore attribute practically all the difference between the ionizations in the two cases to corpuscular radiation excited by the X-radiation. The following Table gives the results obtained :—

TABLE II.

Ionizing radiation : the fluorescent radiation from Ag (series K).

Gas.	Observed Ionization in Chamber with C ends.	Observed Ionization in Chamber with Au ends.	Ionization due to Corpuscular radiation.
$\text{SH}_2 + \text{O}_2$	6.38	15.7	9.32
$\text{SO}_2 + \text{H}_2$	5.74	13.5	7.76

} ratio 1.20

As indicated above, when the ionization-chamber was faced with carbon, there was considerable loss of ionizing corpuscles and of the fluorescent X-radiation from S. The values given in the last column are, however, the relative values of ionization due to the absorption of the same radiation—almost entirely corpuscular radiation. The ratio 1.20 differs little from that produced by X-rays (with the very soft rays set up by these X-rays) in the same two mixtures.

Thus

$\frac{\text{Ionization in } (\text{SH}_2 + \text{O}_2)}{\text{Ionization in } (\text{SO}_2 + \text{H}_2)}$ by Ag X-rays and all secondary rays = 1.165.

$\frac{\text{Ionization in } (\text{SH}_2 + \text{O}_2)}{\text{Ionization in } (\text{SO}_2 + \text{H}_2)}$ by corpuscular (electronic) rays set up by Ag X-rays = 1.20.

* This may be shown from a knowledge of the fluorescent X-radiation from gold. It has been shown experimentally by Kleeman (Proc. Roy. Soc. A, vol. lxxxiv, 1910).

Later experiments by Mr. Philpot give the ratio of ionization by the total absorption of corpuscular radiation in SH_2 and SO_2 as 1.35; while for equal absorptions of Ag X-rays the ratio of ionizations is 1.34.

Many experiments remain to be done with homogeneous X-rays of other penetrating powers, but these results show conclusively that equal absorptions of corpuscular (electronic) rays and any secondary rays due to them are accompanied by unequal ionizations, and that ionization by corpuscular radiation is not atomic. They also show a close connexion, suggesting an absolute equality, between the relative ionizations by X-rays and by their corpuscular (electronic) rays.

(1) Mixtures of air and ethyl bromide in varying proportion.

Ethyl bromide, when subject to Röntgen radiation, is ionized to a much greater extent than light gases at the same pressure and temperature owing to the presence of a constituent element bromine of comparatively high atomic weight.

Owing to this high ionization it is possible to measure with considerable accuracy the change in the ionization due to the admixture of very small quantities of ethyl bromide with air.

In order to obtain the mixture of ethyl bromide and air, a small measured quantity of pure liquid ethyl bromide was introduced through a glass tap into a large closed glass vessel of about $6\frac{1}{2}$ litres capacity, and was allowed to evaporate. After complete evaporation of the liquid, the additional partial pressure of the vapour was observed on an attached manometer. Air was then pumped into the vessel till a pressure of about two atmospheres was reached as indicated by the manometer, when the original temperature was approximately attained. The weights and partial pressures of air and ethyl bromide in the vessel were thus known. The mixture was afterwards allowed to pass slowly from this vessel through the ionization-chamber where the pressure was atmospheric. The partial pressures of air and ethyl bromide in the vessel were then approximately proportional to those in the gas chamber.

The homogeneous X-radiation first used was the fluorescent radiation from copper giving the spectral line of series K. The corpuscular radiation excited by this in the aluminium window and back of the ionization vessel, in this case 3.5 centimetres long, produced ionizations negligible in comparison with the direct ionization of the gas, or at any rate the effect of the ends due to loss or gain of secondary

corpuseular radiation was negligible. The fluorescent X-radiation from the aluminium was also found to affect the results little if at all. (This was seen by covering the inside of the ionization-chamber with a layer of lamp-black sufficiently thick to absorb the fluorescent X-radiation from aluminium. The ionization in air was not affected appreciably).

As it was desired to compare the ionizations produced in different gases by beams of the *same* intensity, corrections were made for the screening of the deeper layers. Thus, if I_g and I_a are the total ionizations in a length l of gas and air respectively, i_g and i_a , the ionization coefficients (defined as the ionization produced per centimetre path in a gas by a radiation of unit intensity, all secondary rays being absorbed), J_0 the intensity of the incident beam, λ_g and λ_a the coefficients of absorption of the radiation in gas and air respectively,

$$\frac{I_g}{I_a} = \frac{\int_0^l i_g J_0 e^{-\lambda_g x} dx}{\int_0^l i_a J_0 e^{-\lambda_a x} dx} = \frac{i_g \left[\frac{1 - e^{-\lambda_g l}}{\lambda_g} \right]}{i_a \left[\frac{1 - e^{-\lambda_a l}}{\lambda_a} \right]}.$$

From this $\frac{i_g}{i_a}$ was determined. The results obtained are given in Table III.

TABLE III.

Ionization-chamber 3.5 cm. long, with Al window and end.
Radiation: the fluorescent X-radiation from Cu (series K).
(Ionization was by the primary and all secondary rays.)

Relative weights of C ₂ H ₅ Br and air.		Partial pressures of C ₂ H ₅ Br and air in cm. of mercury.		Observed ionization in mixture.	Ionization corrected for absorption.	Ionization due to air.	Additional ionization due to C ₂ H ₅ Br.	Ionization due to C ₂ H ₅ Br ÷ partial pressure.
C ₂ H ₅ Br.	Air.	C ₂ H ₅ Br.	Air.					
0.0	100	0.0	76	1.0	1.0	1.0	0.0	...
4.53	95.47	0.94	75.06	1.42	1.43	.99	.44	.47
8.82	91.18	1.90	74.1	1.89	1.91	.97	.94	.49
16.5	83.5	4.00	72.0	2.86	2.92	.95	1.97	.49
29.7	70.3	7.65	68.35	4.55	4.75	.90	3.85	.50
39.7	60.3	11.35	64.65	5.83	6.26	.86	5.40	.48
48.0	52.0	15.0	61.0	7.24	7.84	.81	7.03	.47

Columns 1, 2, 3, and 4 need no explanation except that partial pressures in column 2 were calculated from the weights in column 1, it being assumed for uniformity that the total pressure was always 76 cm. of mercury. The absorption of Cu X-radiation was taken from

$$\lambda = \cdot 000143 p_a + \cdot 00327 p_v,$$

where p_a and p_v are the partial pressures expressed in centimetres of mercury.

Column 5 gives the ionization that would have been produced in the air contained in the gaseous mixture if it had been alone, assuming proportionality with pressure over this small range of pressure.

Column 6 gives the additional ionization due to the admixture of C_2H_5Br with the air, in terms of ionization in air at atmospheric pressure.

Column 7 gives the ratio

$$\frac{\text{additional ionization due to admixture of } C_2H_5Br}{\text{partial pressure of } C_2H_5Br}.$$

A similar series of experiments was made using the fluorescent X-radiation from silver (series K). This radiation is a fairly penetrating radiation and produces a much greater ionization in ethyl bromide relative to air than the soft copper radiation of series K. A more delicate test is therefore possible with the silver radiation. In addition to this, it causes the emission of a well known fluorescent X-radiation from bromine, and an intense accompanying corpuscular radiation, which produce their ionizations in the surrounding gaseous mixture, thus increasing the ionization due to direct action. The ionization due to the fluorescent X-radiation from Br was negligible in these experiments: very little of this radiation was absorbed. There was, however, quite a considerable correction to be made owing to the corpuscular radiation from the aluminium ends of the ionization-chamber, for silver X-radiation (series K) excites an intense corpuscular radiation in aluminium. It will, however, appear from what follows that this corpuscular radiation effect did not appreciably affect the *relative* values. Table IV. gives the results of experiments.

TABLE IV.

Ionization-chamber 3.5 cm. long, with Al window and end.

Radiation: the fluorescent X-radiation from Ag (series K).

[Ionization was by the primary and all secondary rays except Br X-radiation (series K).]

Relative weights of C_2H_5Br & air.		Partial pressures of C_2H_5Br & air in cm. of mercury.		Observed Ionization in mixture.	Ionization corrected for absorption.	Ionization due to air in mixture (air ends to chamber).	Additional Ionization due to C_2H_5Br .	Ionization due to $C_2H_5Br \div$ partial pressure.
0	100	0	76	1.0	1.0	$1-c$	0	
0.85	99.15	0.18	75.82	1.39	1.39	$1-c$	.39	2.2
1.64	98.36	0.34	75.66	1.68	1.68	$1-c$	.68	2.0
2.84	97.16	0.60	75.40	2.20	2.20	$.99(1-c)$	1.21	2.0
3.60	96.40	0.75	75.25	2.72	2.72	$.99(1-c)$	1.74	[2.3]
4.5	95.5	0.94	75.06	3.12	3.13	$.99(1-c)$	2.15	2.3
8.8	91.2	1.9	74.1	5.13	5.16	$.98(1-c)$	4.2	2.2
16.5	83.5	4.0	72.0	8.95	9.04	$.95(1-c)$	8.15	2.0
29.7	70.3	7.65	68.35	16.0	16.3	$.91(1-c)$	15.5	2.0
39.7	60.3	11.35	64.65	22.9	23.5	$.86(1-c)$	22.7	2.0
48.0	52.0	15.0	61.0	29.0	30.0	$.81(1-c)$	29.4	2.0

Columns 1, 2, 3, and 4 give quantities similar to those in Table III., the absorption in this case being given by

$$\lambda = .00135 p_v + .00001 p_a.$$

Column 5 gives the ionization in air of the mixture if there had been no gain of corpuscles from the ends. The ionization due to the end effect is represented by " c ."

Column 6 gives the ionization due to the presence of C_2H_5Br with the air. The values were obtained by taking from the total ionization (column 4), the ionization in air by X-rays (column 5) and the ionization x due to net gain of corpuscular radiation from the ends. The quantity x diminishes with an increase in the quantity of ethyl bromide present, becoming negative for large quantities of ethyl bromide. The quantity " c " was obtained from Sadler's experiments* and x computed from these and a knowledge of ionization in the mixtures. Great inaccuracies in these values would, however, produce very small errors in column 6, so the method of their determination need not be given.

In order to study the relation for very small quantities of the vapour of ethyl bromide, about $\frac{1}{2}$ c.c. of the liquid was introduced into the gas-chamber, and air was forced in to bring the pressure to 2 atmospheres. The mixture was then

* Phil. Mag. March 1910.

slowly led through the ionization-chamber and the ionization determined as before. The mixture in the gas vessel was then diluted by the introduction of more air, and from the initial and final pressures the relative masses and partial pressures of ethyl bromide and air in the ionization-chamber were again calculated. The process of dilution was repeated a number of times with the result given in the upper portion of Table IV. The original quantity of ethyl bromide introduced was determined from the ionization produced in it, thus 2.3 in column 7 was assumed correct for experiment 6, and the others were based on this.

Similar experiments were made with the long ionization-chamber, though the range of pressures was not so great.

TABLE V.

Ionization-chamber 11.5 cm. long, with Al window and end.

Radiation: the fluorescent X-radiation from Ag (series K).

[Ionization was by the primary and all secondary rays except Br X-radiation (series K).]

Relative weights of C_2H_5Br & air.		Partial pressures of C_2H_5Br & air in cm. of mercury.		Observed Ionization in mixture.	Ionization corrected for absorption.	Ionization due to air in mixture (air ends to chamber).	Additional Ionization due to C_2H_5Br .	Ionization due to $C_2H_5Br \div$ partial pressure.
0	100	0	76	1.0	1.0	1-b	0	
4.5	95.5	0.94	75.06	3.12	3.15	.99(1-b)	2.29	2.4
8.8	91.2	1.9	74.1	5.46	5.57	.98(1-b)	4.57	2.4
16.5	83.5	4.0	72.0	9.58	9.92	.95(1-b)	8.96	2.2
29.7	70.3	7.65	68.35	17.6	18.7	.91(1-b)	17.72	2.3
39.7	60.3	11.35	64.65	25.0	27.4	.86(1-b)	26.48	2.3
44.2	55.8	13.2	62.8	29.6	32.9	.84(1-b)	31.9	2.4

It is evident from the very small variations of the values in column 7, that the additional ionization due to the admixture of ethyl bromide with air was, within the errors of experiment, proportional to the quantity of ethyl bromide present in the ionization-chamber, though the partial pressures varied from $\frac{1}{8}$ cm. to 15 cm. of mercury, that is, for mixtures containing various proportions of ethyl bromide and air from 1 in 130 to approximately equal quantities by mass.

The possible error in the measurements of the ionization due to small quantities of ethyl bromide was necessarily greater than that in the values given for larger quantities

but there was evidently no marked deviation from proportionality even with these.

It should be pointed out that the total energy absorbed by the gaseous mixtures is not exactly given by the simple formula $Ap_a + Bp_v$, where p_a and p_v denote the partial pressures of air and vapour respectively, for the bromine fluorescent X-radiation (series K) is absorbed to different extents in the various mixtures. Thus in the dilute mixture between 1 and 2 per cent. only of this radiation was absorbed, while in the strongest, about 7 per cent. was probably absorbed. This difference, however, involves quantities of the order of 1 per cent. or at most of 2 per cent. of the whole energy absorbed, and is consequently inappreciable.

The values given in column 7 of Tables IV. and V. are not on quite the same scale. Those in Table IV. should be divided by $(1-c)$ and those in Table V. by $(1-b)$ in order to compare them both with the ionization in air at 76 cm. of mercury pressure. From Sadler's results $(1-c)=.7$ and $(1-b)=.885$. These values then agree very well considering the possible errors involved in the determination of this end effect.

The constancy of the values in column 7 of Tables III., IV., and V. is remarkable unless quite a large ionization in C_2H_5Br is due to the direct action of X-rays, for when the quantity of ethyl bromide is small, the corpuscular radiations and even exceedingly soft fluorescent X-radiations are absorbed almost entirely by air; and when the quantity of ethyl bromide is large, the absorption of these secondary radiations is, in all probability, approximately half in air and half in ethyl bromide. [We may neglect the change of the ionization owing to secondary rays from air being absorbed in ethyl bromide, as this must be very small in the dilute mixtures owing to the small proportion of the rays so absorbed, and in the stronger mixtures owing to the much greater magnitude of the ionizations due to ethyl bromide.] So that the additional ionization due to the addition of ethyl bromide to air was in these experiments closely proportional to the quantity of ethyl bromide, and did not appear to depend to any appreciable extent on whether the secondary rays were absorbed in air or ethyl bromide. But we have found that the ionization in ethyl bromide is about 40 per cent. greater than that in air for the same absorption of X-rays. Kleeman has also concluded that there is greater ionization in ethyl bromide than in air when the corpuscular (electronic) radiation is completely absorbed in both. If, then, all the X-ray ionization had been due to secondary corpuscular radiation we should have expected an increase

of 15 or 20 per cent. in the values of column 7, with the increased quantity of ethyl bromide. Instead of this it is doubtful if there was an increase of 5 per cent. We are aware that without exact knowledge of the laws of absorption of the corpuscular radiation our conclusions can not be definite. In addition, it is still felt that there may have been incomplete saturation in the mixtures rich in ethyl bromide. Further experiments will be made.

Mixtures of Ethyl Bromide and various gases.

A comparison was made between the additional ionizations due to the admixture of a definite quantity of ethyl bromide with various gases. In order to introduce the same quantity of vapour in each case, the gas was slowly bubbled through liquid ethyl bromide, and then through a long spiral glass tube immersed in ice-cold water. The pressure of the ethyl bromide in the emergent mixture was thus the saturation pressure at 0° C., which is 16.6 cm. of mercury. When the mixture of gas at 59.4 cm. pressure and vapour at 16.6 cm. pressure was raised to approximately atmospheric temperature in the ionization-chamber, while the total pressure was still atmospheric, the partial pressures were of course approximately the same.

The results obtained are tabulated below.

TABLE VI.

Ionizing Radiation : Fluorescent X-radiation (series K) from	Gas.	Length of Ionization- Chamber.	Observed Relative Ionizations.	Relative Ionization corrected for Absorption.	Ionization due to Vapour of C ₂ H ₅ Br.
Cu	Air	3.5 cm.	1	1	
	CO ₂	"	1.5	1.5	
	SH ₂	"	10.1	12.2	
	Air + C ₂ H ₅ Br	"	7.3	7.95	7.15
	CO ₂ + C ₂ H ₅ Br	"	7.2	7.95	6.8
	SH ₂ + C ₂ H ₅ Br	"	13.2	16.6	7.0
Cu	Air	11.5 cm.	1	1	
	H ₂	"	.05		
	O ₂	"	1.4	1.4	
	Air + C ₂ H ₅ Br	"	6.03	8.0	7.2
	H ₂ + C ₂ H ₅ Br	"	6.25	7.9	7.8
	O ₂ + C ₂ H ₅ Br	"	6.32	8.57	7.5
Ag	Air	11.5 cm.	1	1	
	H	"			
	O	"	1.44	1.44	
	Air + C ₂ H ₅ Br	"	37	41.8	41
	H ₂ + C ₂ H ₅ Br	"	39.3	44.3	44.2
	O ₂ + C ₂ H ₅ Br	"	37.4	42.2	41.1

332 *Ionization in Gaseous Mixtures by Röntgen Radiation.*

The addition of ethyl bromide at fairly high pressures to sulphur dioxide was not accompanied by nearly the same increase of ionization as when it was added to air. It was found, however, that a liquid was deposited on the sides of the gas-chamber, and that the gaseous pressure decreased owing to some chemical action. Small quantities of ethyl bromide were subsequently used with the results given below.

[Ag X-rays]	C ₂ H ₅ Br	at 3.75 cm. pressure	when with	air	gave additional ionization	1
"	"	"	"	SO ₂	"	.97
[in other experiments						.96, .98]
[Ag X-rays]	C ₂ H ₅ Br	at 16.6 cm. pressure	when with	air	gave additional ionization	1
"	"	"	"	CO ₂	"	.98
"	"	"	"	SH ₂	"	.945
[Ag X-rays]	CH ₃ I	at 13.3 cm. pressure	when with	air	gave additional ionization	1
"	"	"	"	SH ₂	"	.98

It will be seen from the above results and those in Table VI. column 6, that the additional ionization due to the addition of ethyl bromide or methyl iodide to various gases did not differ by more than 8 per cent. from that when mixed with air, the extreme variation being with hydrogen. With this exception the variations appear within the limits of experimental error. When ethyl bromide was mixed with hydrogen the mass of ethyl bromide was over fifty times that of hydrogen, so we may conclude that practically all secondary rays were absorbed in the ethyl bromide itself. When the ethyl bromide was mixed with air, there were approximately equal masses of air and ethyl bromide to absorb the secondary radiations. From our previous experiments, if all ionization had been due to corpuscular radiation we should have expected a difference much greater than the 8 per cent. observed between the additional ionizations due to the ethyl bromide.

Again, according to the corpuscular ionization hypothesis, the additional ionization due to mixing ethyl bromide with sulphuretted hydrogen might have been expected to be considerably greater than that due to mixing with air. What little difference was observed was in the wrong direction. These experiments have not, however, been made under a sufficient variety of conditions to justify definite conclusions. We believe, however, that they will give a complete answer to the question of primary and secondary ionization effects. These preliminary experiments already suggest much.

Summary.

Experiments on the ionization of gaseous mixtures by homogeneous beams of X-rays have led to the following conclusions :—

Ionization by X-rays is not purely atomic. It depends to a certain extent on the chemical combination of the elements.

Equal absorptions of X-rays and of their secondary rays by different gases are not always accompanied by equal ionizations, though as a rule the deviation from proportionality is not great.

Equal absorptions of corpuscular (electronic) radiation by different gases are not always accompanied by equal ionizations.

The relative ionizations produced by equal absorptions of X-rays in the gases experimented upon are, within small errors of experiment, the same as those produced by the corpuscular radiation excited by the X-rays. The results thus point to the possibility of the relative ionizations in different gases due to the total absorption of X-radiation being identical with those due to corpuscular (electronic) radiation and α radiation.

Preliminary experiments appear to indicate—though we do not accept the results as conclusive—that much of the ionization by X-rays is not due to the secondary corpuscular radiation. Further experiments on these lines will probably give the most direct answer to the question as to the part played by secondary rays in the process of ionization.

XXIX. Intelligence and Miscellaneous Articles.

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN my paper in the December number of the *Phil. Mag.*, there was a footnote on page 875 referring to the work of Rutherford and others which was done more recently than that utilized in the paper. I feel that this footnote, which was hurriedly attached while the paper was in proof, is very inadequate, and wish to express my opinion that pages 875 and 876 of the paper need considerable modification in view of more recent work. This applies, of course, only to the statements concerning the possible varieties of α particle, which were developed only as illustrations of the theory, so that their complete removal would not alter the scope of the theory.

Prof. Rutherford and his collaborators have shown, in so many cases, that the α particle, at any rate soon after birth, is a Helium atom, that these two pages should be read with caution.

I shall be very glad if you can publish this letter, pending a more detailed treatment on which I am at present engaged.

Yours very truly,

Trinity College, Cambridge.

J. W. NICHOLSON.

The University of Melbourne.
25th October, 1911.

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN the Proceedings of the Physical Society, vol. xxiii. part 5, which has just come to hand, I find that on June 9th, 1911, Professor S. P. Thompson read a paper to the Physical Society entitled "A New Method of Approximate Harmonic Analysis by selected Ordinates."

In the Philosophical Magazine for November 1903, I published a "Preliminary Account of a Wave Tracer and Analyser" which I had designed, and which carried out on actual live waves of e.m.f. current, or magnetic flux, the process now brought forward by Professor Thompson. In my paper the theory of this method of Harmonic Analysis was given as bearing on the operation of the Wave Tracer and Analyser, and it was shown that the method was applicable to any periodic curve.

Attention was also drawn to the fact that the method was analogous to that of Wedmore, whose work Professor Thompson does not seem to be acquainted with, but who was the first, so far as I am aware, to apply to Harmonic Analysis the simple method of adding and subtracting selected ordinates.

When using the Wave Tracer and Analyser for magnetic research, I found that it was quicker and more accurate to obtain by its means the complete wave only, by observing a selected number (usually 15) of its equi-spaced ordinates, and afterwards to apply the method of analysis under discussion to these ordinates. Having found the process very satisfactory, I thought the knowledge of it would be useful to others, and on December 8th 1904 I read a paper at the Royal Society of Victoria on "An Expeditious Method of Harmonic Analysis," in which both the theory and my practice of the method was fully explained. This paper was afterwards printed in the Philosophical Magazine for January 1906.

Professor Thompson has certainly modified the practical application of the method by an elegant device, *i. e.* of determining two ordinates in quadrature for each harmonic, thus obtaining their amplitudes and phases by a method different from mine, but in this no new principle is involved.

Though I dislike raising questions of priority, I feel that the title of Professor Thompson's paper is so misleading as to render this letter necessary, for his method is not new but involves, at most, an improvement on an old established method.

Yours faithfully,

THOMAS R. LYLE.

To the Editors of the *Philosophical Magazine*.

GENTLEMEN,—

By your courtesy I am able to reply to the matter raised by Professor Lyle, whose work in Harmonic Analysis with his Wave-Tracer and Analyser is well known to me. It is probably due to the width of ocean which divides us that any misunderstanding can have arisen. He suggests that I am not aware of Mr. Wedmore's still earlier method of 1896. At that date Mr. Wedmore was a valued member of my staff; and I had every reason to know the detail of his work. The essential points of difference between Professor Lyle's process and mine appear to be these. He takes one set of selected ordinates ("usually fifteen," he says) to determine the analysis of the curve and to discover its harmonics; whereas I take different numbers of selected ordinates for each harmonic which I wish to determine. For each harmonic, with his ingenious machine which electrically reverses the sign of the successive ordinates and then adds them, he is able to determine the amplitude directly by rocking the contacts so as to attain the maximum reading, and so deduce the amplitude of the harmonic. In my method this is not applicable in the slightest degree; for in the graphic and arithmetical processes one cannot rock the templates by which the ordinates are selected and measured, to such a position as to give off-hand a maximum average value. Hence in my process it is *essential* to determine separately the sine and cosine components of each harmonic.

In Professor Lyle's process (as also in mine) the presence of any higher harmonic of an order that is any odd number of times the frequency affects the result, and must if present be separately evaluated and eliminated by subtraction. Hence it seems to me that his process, which does not separate the sine and cosine components, will be in error if there is any difference of phase between the harmonic that is being determined and the higher harmonic present: for the position of maximum attained by the rocking of the contacts takes no account of such difference of phase. I ought in justice to add that another prior worker in this field, Dr. Fischer-Hinnen, whose memoir is mentioned amongst the references in my paper, did determine separately the sine and cosine components, though he gave no theory of the process. But, indeed, the separate determination of sine and cosine components is as old as Fourier. A point of novelty in Prof. Lyle's electrical process was the avoidance of this very feature. A very simple consideration shows that the characteristic method of Fourier's analysis is the multiplication of every ordinate by the sine or cosine of the angle at which it stands (or by some multiple of that angle corresponding to the order of the harmonic sought), prior to integrating. My process is equivalent to selecting only those ordinates for which the sine or cosine needed in the multiplication is either $+1$ or -1 ; hence the integration is effected by mere addition and subtraction; hence also it comes back to being a particular case of Fourier's method.

I am, &c.,

SILVANUS P. THOMPSON.

Jan. 27, 1912.

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

Freiburg i. Br., 22 Dec., 1911.

IN vol. xxii. of the Philosophical Magazine, Dec. 1911, p. 922, Mr. Rossi, starting from Ritz's Theory (*Ann. der Phys.* 1908), makes some interesting observations on a relation between the atomic volumes and the spectra of elements. May I be allowed to state that I obtained similar results in 1904, which were published in the *Physikalische Zeitschrift*, v. p. 302. From the experiments of Kayser and Runge, it was shown that the limits ν_0 of the branch series for each group of the periodic system are shifted further towards the red end of the spectrum the greater the atomic weight. I started with the supposition that the limits were not only dependent on the atomic weight, but also on the atomic volume (*i. e.* lineal dimensions of the atoms), and I was surprised to find that the limits can be represented as functions of the atomic volume alone. So far my results are in perfect agreement with those of Mr. Rossi.

The following which I obtained was not observed by him, but it is well shown in fig. 1 of his paper: that the monovalent elements Cu and Ag fall roughly into the same line as the monovalent alkali elements, with which they are nearly related in the periodic system. Similarly the divalent elements Zn, Cd, Hg also fall into the same line with those of the divalent elements of the alkaline earths, *viz.* Mg, Ca, Sr.

It is scarcely necessary for me to say that Mr. Rossi's result, that the log of the limits of the branch are lineally connected with the log of the atomic volumes, was already known to me, forming the starting-point of my calculations, as can be seen in my figure. I should, however, like to state that Mr. Rossi's interesting result on the different inclinations of the lines of the nearly related elements was not remarked by me, and that in consequence I regard his work as a considerable addition to our knowledge of the subject.

Finally, I may add that in 1903 W. Ritz has published another theory of the spectrum-lines (*Ann. der Phys.* xii. p. 264). From this work also the influence of the lineal dimensions of the atom on the limits ν_0 can be inferred, as Ritz imagined we have to do with vibrations of square surfaces where the frequencies depend, amongst other things, on the length of the sides of the squares. In my work, however, I started from more general considerations.

I am,

Yours sincerely,

M. REINGANUM.

FIG. I.

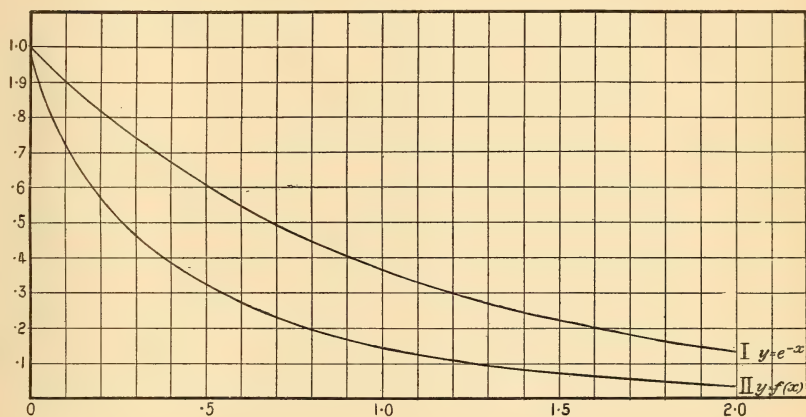
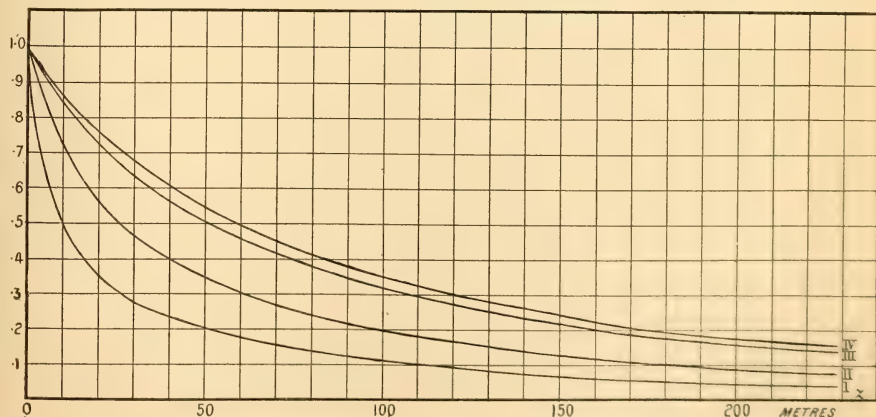
Curves of the functions I. $y=e^{-x}$.II. $y=f(x)=e^{-x}+x \operatorname{Ei}(-x)$.

FIG. II.

Decrease of intensity of penetrating radiation with height above the earth's surface. Intensity at surface is taken as unity. The various curves refer to intensities due to radioactive material in layers of different thickness.

Curve I. $h=.01$ cm.Curve III. $h=1.1$ cm.Curve II. $h=.11$ cm.Curve IV. $h=11$ cm.

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

MARCH 1912.

XXX. *The Asteroids.* By PERCIVAL LOWELL*.

1. **W**HEN the zone of minor planets circling between the orbits of Mars and Jupiter is tabulated with regard to the mean distances of its members from the Sun, certain gaps in the arrangement become apparent. Kirkwood was the first to point out the significance of these gaps by showing that they occurred at just the points where a minor planet would have a period commensurable with that of Jupiter, and he attributed them in consequence to the perturbing action of that great body. The question then arose as to whether the gaps were permanent or effects only of a libratory action due to Jupiter which Laplace had already discovered in the case of Jupiter's satellites I., II., and III. Basing an argument on this principle Newcomb gave it as his opinion that the latter was the case, and that the action was not permanent but merely the pendulum-like swing due to what Laplace had explained. This opinion has been followed by others, and the same argument has recently been advanced as affecting the secular results due to commensurability in the periods of the major planets. It will be proper, therefore, to begin what we have to say about the asteroids by showing that a more careful consideration of the pendulum argument discloses that it is itself illusory.

One difficulty in celestial mechanics lies in the fact that

* Communicated by the Author.

Phil. Mag. S. 6. Vol. 23. No. 135. March 1912. 2 A

the integrals in the problem of three bodies cannot be rigorously solved, and have to be expressed in series, so that the result obtained depends upon the number of terms included. Secondly, Poincaré has latterly shown that the series used by astronomers become eventually divergent so that in time they cease to represent the action at all. Finally, whereas Laplace and Lagrange thought they had established the eventual stability of the solar system, by proving that so far as terms to the first order in the masses are concerned there was no secular variation of the major axes, it has since been demonstrated that in those of the second order in the masses terms of the form $t \cos \theta$ and $t \sin \theta$ arise, called from their discoverer Poisson terms, and by Haretu that in the third order terms in which t is explicitly represented make their appearance. So that we can no longer assert the secular non-variability of the major axes.

These two points : that it is never safe to argue from a single term, and that we can no longer assume the major axes to be in the long run invariable, entirely vitiate deductions too hastily drawn from the pendulum effect discovered by Laplace. Furthermore, it appears that the received criterion for libration does not hold throughout the action. This will be seen when we examine the subject analytically.

Tisserand, in his excellent exposé in his *Mécanique Céleste* and elsewhere, discusses only the case where Jupiter's orbit is supposed circular. Callandreau does the same. Further-

more, Tisserand neglects the term $\frac{d\varpi}{dt}$ as being negligible, which turns out not to be the case.

2. We shall now investigate the subject with more particularity. In so doing we shall find that libration does not account for the gaps in the asteroid belt nor in the rings of Saturn, nor, finally, for the entire lack of commensurability in the periods of all the major planets.

We will begin by consideration of the case of asteroids travelling at a mean distance from the Sun such as to make their mean motions nearly twice that of Jupiter, those, therefore, in the neighbourhood of the gap $n=2n'$. We shall not assume Jupiter's orbit circular, but shall take the ellipticity of that orbit into account, designating everything relating to Jupiter by a dash ; the elements of the asteroid being unaccented.

The terms of the perturbing function which are important in the case are those dependent on the argument $l-2l'$. We

shall neglect the inclinations of the asteroids' orbits. Their inclusion would introduce terms only of the second order in e or less, assuming η to be of the order of e . The perturbing function is thus composed of terms as follows:—

$$\begin{aligned} R = & \text{secular terms} + A \cos \theta + A_1 \cos 2\theta + A_2 \cos 3\theta \text{ \&c.} \\ & + B \cos \theta' + B_1 \cos 2\theta' + B_2 \cos 3\theta' \text{ \&c.} \\ & + \text{terms with other combinations of} \\ & \quad \varpi - \varpi' \text{ with } \theta \text{ or } \theta', \end{aligned}$$

$$\text{in which} \quad \theta = \int n dt + \epsilon - \int 2n' dt - 2\epsilon' + \varpi,$$

$$\text{and} \quad \theta' = \int n dt + \epsilon - \int 2n' dt - 2\epsilon' + \varpi'.$$

We will consider first the two most important terms, $A \cos \theta$ and $B \cos \theta'$. The second term introduces the action due to Jupiter's orbital eccentricity.

Using the usual symbols of Laplace and Leverrier we have then

$$(1) \quad R = -\frac{k^2 e m'}{2a'} (4b^{(2)} + b_1^{(2)}) \cos \theta + \frac{e' k^2 m'}{2a'} (3b^{(1)} + b_1^{(1)}) \cos \theta',$$

in which the subscripts in the b 's denote $\alpha \frac{db^{(i)}}{d\alpha}$.

Now θ' may be written

$$\begin{aligned} \theta' &= \int n dt + \epsilon - \int 2n' dt - 2\epsilon' + \varpi - \varpi + \varpi' \\ &= \theta - (\varpi - \varpi'), \end{aligned}$$

whence

$$\begin{aligned} R = -\frac{k^2 m'}{2a'} \left\{ [e(4b^2 + b_1^{(2)}) - e'(3b^{(1)} + b_1^{(1)}) \cos(\varpi - \varpi')] \cos \theta \right. \\ \left. - \{e'(3b^{(1)} + b_1^{(1)}) \sin(\varpi - \varpi')\} \sin \theta \right\}. \end{aligned}$$

Let the quantity in the first bracket be $h' - h'' \cos(\varpi - \varpi')$; that in the second, $h'' \sin(\varpi - \varpi')$.

Since

$$\begin{aligned} \theta &= \int n dt + \epsilon + \varpi - \int 2n' dt - 2\epsilon', \\ (2) \quad \frac{d^2 \theta}{dt^2} &= \frac{dn}{dt} + \frac{d^2 \epsilon}{dt^2} + \frac{d^2 \varpi}{dt^2} - 2 \frac{dn'}{dt} - 2 \frac{d^2 \epsilon'}{dt^2}. \end{aligned}$$

The second and third members of the right side are

multiplied by m'^2 , and are therefore a thousand times smaller than $\frac{dn}{dt}$. The fourth and fifth are multiplied by m , which is evanescently small. We thus get

$$\frac{d^2\theta}{dt^2} = \frac{dn}{dt}.$$

Now

$$\frac{dn}{dt} = -\frac{3}{\alpha^2} \frac{dR}{d\epsilon},$$

whence (2)

$$\frac{d^2\theta}{dt^2} = -\frac{3}{2} \frac{k^2 m'}{\alpha^2 \alpha'} \left\{ \{h' - h'' \cos(\varpi - \varpi')\} \sin \theta + h'' \sin(\varpi - \varpi') \cos \theta \right\}.$$

For k^2 put its value, $n^2 \alpha^3$, and let

$$3n^2 m' \alpha \{h' - h'' \cos(\varpi - \varpi')\} = h_1$$

and

$$3n^2 m' \alpha h'' \sin(\varpi - \varpi') = h_2.$$

Then $\frac{d^2\theta}{dt^2}$ may be put in the form

$$\frac{d^2\theta}{dt^2} = -\frac{1}{2} \sqrt{(h_1^2 + h_2^2)} \sin(\theta - \gamma),$$

where

$$\tan \gamma = \frac{-h_2}{h_1}.$$

Multiply both sides by $2 \frac{d\theta}{dt}$ and integrate,

$$\begin{aligned} \left(\frac{d\theta}{dt}\right)^2 &= \sqrt{(h_1^2 + h_2^2)} [\cos(\theta - \gamma) + c] \\ &= \frac{1}{2} A [\cos(\theta - \gamma) + c], \end{aligned}$$

if

$$A = 2 \sqrt{(h_1^2 + h_2^2)},$$

whence (3)

$$\frac{d\theta}{dt} = \sqrt{\frac{1}{2} A [\cos(\theta - \gamma) + c]}.$$

The action depends upon the value of the constant c . If A is positive and c is negative and greater than unity $\frac{d\theta}{dt}$ becomes imaginary for all values of $\theta - \gamma$.

(1) If c is positive and greater than one $\frac{d\theta}{dt}$ is real and never changes sign. Consequently the action is continuously in one direction and increases or decreases indefinitely.

(2) If c , irrespective of sign, is less than unity and A is negative, $\frac{d\theta}{dt}$ becomes imaginary for values of $\theta - \gamma$ around 0° .

$\theta - \gamma$ is consequently oscillatory about 180° ; unevenly so in consequence of γ .

(3) If c , irrespective of sign, is less than unity and A positive, $\frac{d\theta}{dt}$ becomes imaginary for values of $\theta - \gamma$ near 180° .

$\theta - \gamma$ is consequently similarly oscillatory around 0° .

Case (1) is the usual one in celestial mechanics.

Case (2) finds interesting exemplification in Jupiter's satellites I., II., and III. and in Hyperion perturbed by Titan.

Case (3) has apparently been exemplified in the cases of Enceladus and Dione and in the inclinations by Mimas perturbed by Tethys.

5. Let us now consider this equation :

$$\frac{d\theta}{dt} = \sqrt{\frac{1}{2} A (\cos \theta + c)}.$$

To begin with, the right side of it demands attention. In it n and n' may without loss of accuracy be taken as constant. And here a simplification may be introduced.

Since

$$n^2 a^3 = k^2 \quad \text{and} \quad n'^2 a'^3 = k^2 (1 + m'),$$

if we denote the mass of the Sun by unity, we may for a first criterion take

$$n^2 a^3 = n'^2 a'^3 \quad \text{inasmuch as} \quad m' = \frac{1}{1047.35},$$

and furthermore calculate

$$\alpha = \frac{a}{a'}$$

with the values of a and a' corresponding to

$$n = 2n' \quad \text{or} \quad \alpha = \frac{1}{\sqrt[3]{4}}.$$

This will usually suffice to determine the character of the action. Where the result of the two sides is close we must use the true values of n , which are found from

$$\alpha = \frac{a}{a'} = \frac{n'^{2/3}}{n^{2/3}} \sqrt[3]{\frac{1}{1 + m'}}$$

6. Taking up now the terms in 2θ , 3θ , &c., $2\theta'$, $3\theta'$, &c., we find that their expressions are as follows:—

$$\begin{aligned}
 (4) \quad R = & \frac{k^2 m'}{a'} \times \\
 & \left[-\frac{e}{2} (4b^{(2)} + b_1^{(2)}) \cos \theta \right. \\
 & - \left(\frac{e}{2} \right)^3 \left(-14 b^{(2)} - \frac{5}{2} b_1^{(2)} + 3 b_2^{(2)} + \frac{1}{2} b_3^{(2)} \right) \cos \theta \\
 & + \frac{e}{2} \left(\frac{e'}{2} \right)^2 \{ 64 b^{(2)} + 6 b_1^{(2)} - 8 b_2^{(2)} - b_3^{(2)} \} \cos \theta \\
 & + \frac{e'}{2} \{ 3 b^{(1)} + b_1^{(1)} \} \cos \{ \theta - (\varpi - \varpi') \} \\
 & + \left(\frac{e}{2} \right)^2 \frac{e'}{2} \{ -12 b^{(1)} + 4 b_1^{(1)} + 7 b_2^{(1)} + b_3^{(1)} \} \cos \{ \theta - (\varpi - \varpi') \} \\
 & + \left(\frac{e'}{2} \right)^3 \{ -14 b^{(1)} + 2 b_1^{(1)} + \frac{9}{2} b_2^{(1)} + \frac{1}{2} b_3^{(1)} \} \cos \{ \theta - (\varpi - \varpi') \} \\
 & - \left(\frac{e}{2} \right)^2 \frac{e'}{2} \left\{ \frac{105}{2} b^{(-3)} + \frac{19}{2} b_1^{(-3)} - \frac{7}{2} b_2^{(-3)} - \frac{1}{2} b_3^{(-3)} \right\} \cos \{ \theta + (\varpi - \varpi') \} \\
 & - \frac{e}{2} \left(\frac{e'}{2} \right)^2 \{ 5 b_1^{(0)} + 4 b_2^{(0)} + \frac{1}{2} b_3^{(0)} \} \cos \{ \theta - 2(\varpi - \varpi') \} \\
 & + \left(\frac{e}{2} \right)^2 \{ 22 b^{(4)} + 7 b_1^{(4)} + \frac{1}{2} b_2^{(4)} \} \cos 2\theta \\
 & - \frac{e}{2} \frac{e'}{2} \{ 42 b^{(3)} + 14 b_1^{(3)} + b_2^{(3)} \} \cos \{ 2\theta - (\varpi - \varpi') \} \\
 & + \left(\frac{e'}{2} \right)^2 \{ 19 b^{(2)} + 7 b_1^{(2)} + \frac{1}{2} b_2^{(2)} \} \cos \{ 2\theta - 2(\varpi - \varpi') \} \\
 & - \left(\frac{e}{2} \right)^3 \{ 134 b^{(6)} + \frac{93}{2} b_1^{(6)} + 5 b_2^{(6)} + \frac{1}{6} b_3^{(6)} \} \cos 3\theta \\
 & + \left(\frac{e}{2} \right)^2 \frac{e'}{2} \left\{ \frac{825}{2} b^{(5)} + \frac{291}{2} b_1^{(5)} + \frac{31}{2} b_2^{(5)} + \frac{1}{2} b_3^{(5)} \right\} \cos \{ 3\theta - (\varpi - \varpi') \} \\
 & - \frac{e}{2} \left(\frac{e'}{2} \right) \{ 416 b^{(4)} + 151 b_1^{(4)} + 16 b_2^{(4)} + \frac{1}{2} b_3^{(4)} \} \cos \{ 3\theta - 2(\varpi - \varpi') \} \\
 & + \left(\frac{e'}{2} \right)^3 \{ 136 b^{(3)} + 52 b_1^{(3)} + \frac{11}{2} b_2^{(3)} + \frac{1}{6} b_3^{(3)} \} \cos \{ 3\theta - 3(\varpi - \varpi') \} \left. \right].
 \end{aligned}$$

To determine the value of the right side in this case we

may substitute $\frac{dR}{d\epsilon}$ got from the longer expression for that obtained previously for the shorter in $\frac{d^2\theta}{dt^2}$ and integrate term by term. After which we evaluate each term separately and extract the square root of the result.

7. The effect of these terms depends upon the values of θ , $\varpi - \varpi'$, and e . If $\theta = 180^\circ$ approximately and also $\varpi - \varpi' = 180^\circ$ approximately, the aggregate of the terms depending on θ becomes as large as possible; the terms in 2θ add to it whatever the value of e , while the terms in 3θ do likewise. They are, however, smaller unless e be very large.

If $\theta = 180^\circ$ approximately and $\varpi - \varpi' = 0$ approximately the aggregate of the terms in θ is smaller than it otherwise would be; the terms in 2θ add to it if e be large, but subtract from it if e be small. Those in 3θ do the same.

8. Turning now to the other side of the inequality

$$\frac{d\theta_1}{dt} \approx n_1 - 2n' + \frac{d\epsilon_1}{dt} + \frac{d\varpi_1}{dt},$$

the subscripts being introduced to denote that the elements are taken at the epoch of osculation, the several terms are

$$n_1 - 2n',$$

where $n' = 299'' \cdot 128$ a day, and n_1 varies from the double of this by a few seconds for the asteroids considered. Twenty-five seconds is as far as it is necessary to go. The second term is

$$\frac{d\epsilon}{dt} = -\frac{2}{na} \cdot \frac{dR}{da} + \frac{\sqrt{1-e^2}}{na^2e} \{1 - \sqrt{1-e^2}\} \cdot \frac{dR}{de} + \frac{\tan^2 \frac{i}{2}}{na^2\sqrt{1-e^2}} \cdot \frac{dR}{di}.$$

Now

$$\frac{d(4b^{(2)} + b_1^{(2)})}{da} = \frac{d\left(4b^{(2)} + \alpha \frac{db^{(2)}}{d\alpha}\right)}{da} = \frac{d\left(4b^{(2)} + \alpha \frac{db^{(2)}}{d\alpha}\right)}{d\alpha} \frac{d\alpha}{da},$$

which since

$$\frac{d\alpha}{da} = \frac{1}{a'},$$

$$= \frac{1}{a} (5b_1^{(2)} + b_2^{(2)}),$$

whence

$$\frac{dR}{da} = -\frac{n^2 a^3 m}{2aa'} \left[e(5b_1^{(2)} + b_2^{(2)}) \cos \theta - b_1^{(0)} \right].$$

Also

$$\begin{aligned} \frac{dR}{de} = \frac{n^2 a^3 m'}{2a'} \left[e(b_1^{(0)} + \frac{1}{2} b_2^{(0)}) + e' \left[(b^{(1)} - \alpha) - (b_1^{(1)} - \alpha) - \frac{1}{2} b_2^{(1)} \right] \cos(\varpi - \varpi') \right. \\ \left. - (4b^{(2)} + b_1^{(2)}) \cos \theta + e(22b^{(4)} + 7b_1^{(4)} + \frac{1}{2} b_2^{(4)}) \cos 2\theta \right. \\ \left. - \frac{3}{4} e^2 (134b^{(6)} + \frac{93}{2} b_1^{(6)} + 5b_2^{(6)} + \frac{1}{6} b_3^{(6)}) \cos 3\theta \right], \end{aligned}$$

and

$$\frac{dR}{di} = -\frac{n^2 a^3 m' \alpha}{4a'} \left\{ \sin i c^{(-1)} - \sin i c^{(3)} \cos [2\theta - 2\varpi + 2\tau'] \right\} + \&c.,$$

giving finally

$$(4) \quad \frac{d\epsilon}{dt} = n\alpha m' \left[e(5b_1^{(2)} + b_2^{(2)}) \cos \theta - b_1^{(0)} - \frac{1}{4} e(4b^{(2)} + b_1^{(2)}) \cos \theta \right. \\ \left. + \frac{1}{2} (b_1^{(0)} + \frac{1}{2} b_2^{(0)}) \tan \frac{i}{2} \tan i \sec^2 i + \text{periodic terms in } i \right].$$

9. Similarly

$$\begin{aligned} \frac{d\varpi}{dt} = \frac{\sqrt{1-e^2}}{na^2 e} \frac{dR}{de} + \frac{\tan \frac{i}{2}}{na^2 \sqrt{1-e^2}} \frac{dR}{di} \\ (5) = \frac{n\alpha m'}{2} \left\{ (b_1^{(0)} + \frac{1}{2} b_2^{(0)}) + \frac{e'}{e} \left[(b^{(1)} - \alpha) - (b_1^{(1)} - \alpha) - \frac{1}{2} b_2^{(1)} \right] \cos(\varpi - \varpi') \right. \\ \left. - \frac{1}{e} (4b^{(2)} + b_1^{(2)}) \cos \theta + (22b^{(4)} + 7b_1^{(4)} + \frac{1}{2} b_2^{(4)}) \cos 2\theta \right. \\ \left. + \frac{1}{2} e(4b^{(2)} + b_1^{(2)}) \cos \theta - \frac{3}{4} e(134b^{(6)} + \frac{93}{2} b_1^{(6)} + 5b_2^{(6)} + \frac{1}{6} b_3^{(6)}) \cos 3\theta \right. \\ \left. + (b_1^{(0)} + \frac{1}{2} b_2^{(0)}) \tan \frac{i}{2} \tan i \sec^2 i + \text{periodic terms in } i \right\}, \end{aligned}$$

omitting throughout terms in e^2 or ee' , and certain terms in e' .

Calculation shows that the terms introduced by $\frac{dR}{di}$ are all practically insensible in $\frac{d\varpi}{dt}$. And this for two reasons.

The term

$$\frac{1}{na^2 e} \frac{dR}{de}$$

is bigger than

$$\frac{\tan \frac{i}{2}}{na^2 \sqrt{1-e^2}} \frac{dR}{di}$$

both because the former is divided by e and because the latter is originally at least one degree higher in e or its equivalent $\tan \frac{1}{2}i$. For the asteroids $e = \sin \phi$ and $\sin \frac{1}{2}i$ [which is approx. $\sin \frac{1}{2}\gamma$ where γ in Leverrier's notation signifies the mutual inclination of the orbits] $= \eta$ are of the same order of magnitude, the last being indeed on the average about half as large only as the other.

Owing to this divisor e the term in $\frac{d\varpi}{dt}$,

$$\frac{1}{na^2e} \frac{dR}{de},$$

is introduced with a large numerical coefficient, to the result that instead of being negligible with regard to $n - 2n'$ it sometimes, as in the case of (286), actually exceeds the latter.

10. Resuming now the equation

$$\frac{d\theta}{dt} = \sqrt{\frac{1}{2}A[\cos(\theta - \gamma) + e]},$$

if we put for $\cos(\theta - \gamma)$ its value

$$= 2 \cos^2 \frac{1}{2}(\theta - \gamma) - 1,$$

we have for the criterion that libration cannot occur

$$(6) \quad \frac{d\theta}{dt} > \sqrt{A} \cos \frac{1}{2}(\theta - \gamma),$$

since in this case e must not exceed 1.

A depends, it will be noticed, not upon e alone, as in Tisserand's formula, but upon e' as well; while γ introduces $\varpi - \varpi'$.

11. Applying this criterion to the several asteroids on both sides of the gap $n = 2n'$ we have the following Tables I. and II.

In this and the subsequent tables $\frac{d\theta}{dt}$ and $\sqrt{A} \cos \frac{1}{2}(\theta - \gamma)$ have been calculated for all the asteroids where inspection showed any possibility of libration. The apparent omissions indicate that no libration occurs. L stands for libration in the last column.

TABLE I.

	θ .	$\varpi - \varpi'$.	$n_1 - 2n$.	ϕ .	$\frac{d\epsilon}{dt}$.	$\frac{d\varpi}{dt}$.		$\frac{d\delta}{dt}$.	$\sqrt{A}$.	$\sqrt{A} \cos \frac{1}{2}(\theta - \gamma)$.	
						secular.	periodic.				
680	178° 38'	265° 51'	25.9	16° 10'							
154	118 11	...	26.1	5 2							
92	62 57	...	24.4	5 23							
184	204 33	...	24.2	3 28	...	...	-6''.3				
436	355 30	...	23.8	4 46							
465	188 56	...	23.9	13 46							
618	196 9	...	23.8	3 27							
286	191 34	20 3	22.4	0 46	-''26	-''36*	+31.00				
381	310 35	...	22.4	7 15							
491	124 30	...	22.3	3 43							
595	6 58	...	21.9	4 18							
580	13 54	42 4	20.3	7 39	.05	.21	-2 .00	18''.61	19''.01	18''.81	L
667	151 46	85 32	19.8	9 49							
300	63 19	312 47	19.0	2 27	...	...	-4 .4	14 .6	10 .1		
108	20 50	151 59	19.6	6 1	-.02	.33	-2 .80	17 .16	19 .13	18 .69	L
325	234 26	47 11	18.7	9 9							
581	36 12	50 43	17.7	2 31	-.16	.13	-7 .21	10 .47	10 .41	9 .11	
318	103 52	63 34	17.8	3 36	...	...	+1 .6	...	13 .3		
122	319 4	177	16.1	3 11	-.14	.43	-5 .44	10 .95	14 .87	14 .02	L
530	167 53	305 42	13.7	10 27							
175	164 4	315 3	13.0	11 4	...	...	...	...	23 .31	4 .16	
1/2	Period	of	Jupiter.								

* Taking i into account -''39.

TABLE II.

	θ .	$\varpi - \varpi'$.	$n_1 - 2n'$.	ϕ .	$\frac{d\epsilon}{dt}$.	$\frac{d\varpi}{dt}$.		$\sqrt{A}$.	$\sqrt{A} \cos \frac{1}{2}(\theta - \gamma)$.
						secular.	periodic.		
1/2	Period	of	Jupiter.						
401	212° 48'	223° 13'	14.95	2° 40'	.1	+ .47	+8.02	13''.77	-2.49
525	151 58	34 35	16.9	21 47	...	...	...	33 .04	7.2
643	235 57	77 20	20.7	4 26					
566	197 15	12 6	20.9	6 55					
466	143 45	182 15	21.5	4 45					
168	185 51	11 7	26.6	4 22					
225	335 55	285 43	30.7	15 18	...	...	-3.30		
528	212 22	16 46	31.9	1 8					
319	44 48	32 36	34.3	12 16					
420	146 10	90 1	34.6	2 32					
229	94 59	321 8	35.8	8 10					

From the results of these tables we perceive that only three of the asteroids in the $n=2n'$ gap, to wit (122), (108), and (580), show libration. Whereas were the asteroids as uniformly distributed throughout the $n=2n'$ gap as they are on both sides of it, we ought to find 40 or more where we now find none. As the gaps throughout the whole asteroid zone occur where and only where their periods are commensurable with that of Jupiter—up to those involving the seventh power of the eccentricities—we see that the arrangement cannot be fortuitous, and furthermore from the present investigation that permanent not libratory action is necessary to account for it.

12. We now take up the case of the gap $n=3n'$. For this R becomes for the terms in θ , θ' , and θ'' , all of which are reducible to θ ,

$$(7) \quad R = \frac{k^2 m'}{8a'} \times$$

$$\left\{ \begin{aligned} & [e^2(21b^{(3)} + 10b_1^{(3)} + b_2^{(3)}) - ee(40b^{(2)} + 20b_1^{(2)} + 2b_2^{(2)})\cos(\varpi - \varpi')]] \cos \theta \\ & - [ee'(40b^{(2)} + 20b_1^{(2)} + 2b_2^{(2)})\sin(\varpi - \varpi')] \sin \theta \\ & + [e'^2[17(b^{(1)} - \alpha) + 10(b_1^{(1)} - \alpha) + b_2^{(1)}] \cos 2(\varpi - \varpi')] \cos \theta \\ & + [e'^2[17(b^{(1)} - \alpha) + 10(b_1^{(1)} - \alpha) + b_2^{(1)}] \sin 2(\varpi - \varpi')] \sin \theta \end{aligned} \right\}$$

$$\text{Letting} \quad h' = e^2[21b^{(3)} + 10b_1^{(3)} + b_2^{(3)}],$$

and

$$h'' = ee'[40b^{(2)} + 20b_1^{(2)} + 2b_2^{(2)}]$$

$$h''' = e'^2[17(b^{(1)} - \alpha) + 10(b_1^{(1)} - \alpha) + b_2^{(1)}],$$

we get in this case, by a process similar to that for $n=2n'$,

$$\frac{d\theta}{dt} = \sqrt{-\frac{1}{2}A(\cos(\theta - \gamma) + c)},$$

in which

$$A = \frac{k^2 m'}{8a'} \sqrt{[\{h' - h'' \cos(\varpi - \varpi') + h''' \cos 2(\varpi - \varpi')\}^2 + \{h'' \sin(\varpi - \varpi') - h''' \sin 2(\varpi - \varpi')\}^2]}.$$

This equation in $\frac{d\theta}{dt}$ can be put in the form

$$(9) \quad \frac{d\theta}{dt} = \sqrt{A} \sin \frac{1}{2}(\theta - \gamma) \quad \text{or} \quad = \sqrt{A} \cos \frac{1}{2}(\theta - \gamma),$$

according to the sign of A.

If A is plus

$$-\cos(\theta - \gamma) = 2 \sin^2 \frac{1}{2}(\theta - \gamma) - 1,$$

if minus

$$\cos(\theta - \gamma) = 2 \cos^2 \frac{1}{2}(\theta - \gamma) - 1.$$

14. Following are the tables for the gap $n = 3n'$.

TABLE III.

	θ .	$\varpi - \varpi'$.	$n_1 - 2n$.	ϕ .	$\frac{d\epsilon}{dt}$.	$\frac{d\varpi}{dt}$.		$\sqrt{A}$.	$\sqrt{A} \cos \frac{1}{2}(\theta - \gamma)$.	
						secular.	periodic.			
650	117° 13'	18° 54'	21.1	10° 46'						
474	316 55	292 56	19.3	8 27				8''·2		
556	224 45	88 11	18.4	5 47						
248	311 5	234 59	16.5	3 41						
17	136 27	250 15	16.2	7 40				9.5		
335	162 47	275 57	15.3	10 22	...	·23*	-·75*	10.5		
329	266 12	204 14	14.7	1 36						
495	208 44	13 40	12.7	8 28	...	...	-·32	4.1		
132	85 48	139 48	6.3	19 21	-·10	...	-·08	20.6	15''·8	L
1/3	Period	of	Jupiter.							

* Only important terms included.

TABLE IV.

	θ .	$\varpi - \varpi'$.	$n_1 - 2n$.	ϕ .	$\frac{d\varpi}{dt}$.	$\sqrt{A}$.
					periodic.	
1/3	Period	of	Jupiter.			
619	148° 2''	349° 36'	10.8	4° 18'	+ ''·41*	4''·2
518	314 20	309 40	11.6	12 42	+ ·51	5.5
46	143 32	341 34	12.9	9 38	...	4.7
292	305 15	317 54	16.7	1 41		
421	6 48	21 13	18.4	17 1	...	10.6
660	287 54	251 10	19.4	5 53	- ·15	7.9
355	182 46	...	20.1	6 13		
472	273 28	...	21.7	5 38		
89						

* Only the important terms in this column considered.

From the table we see that but one asteroid (132) fulfils the criterion for libration. It will also be noticed that it falls on the sunward side of the gap, as is also the case with the

three fulfilling the criterion in the gap $n=2n'$. This gap then, also, cannot be explained by libratory action.

15. We shall now proceed to show that the criterion, though theoretically correct so far as the terms we have considered go, does not hold throughout the action. To see this we may notice that theoretically the libration is possible to any angle short of 180° from the mid-point dependent only upon the values at the epoch of osculation of $\frac{d\theta}{dt}$ and A . And calculation shows that this angle decidedly exceeds 90° in the case of (122), (108), and (132), that angle being β where

$$(10) \quad \left(\frac{d\theta}{dt}\right)^2 = \frac{1}{2} A [\cos(\theta - \gamma) - \cos \beta].$$

But if $\theta - \gamma = \alpha$, the right side of the criterion vanishes, so that at some point the criterion may state that there is libration, whereas at an earlier stage of the action it stated the contrary. This means that a libration in the case is not a true libration, but seeming such within limits only, to be replaced later on by continuous movement of $(\theta - \gamma)$.

16. That this is actually exemplified by the asteroids we shall perceive from the following table of the elements of (122) for various epochs since its discovery.

TABLE V.

(122)	θ .	ϖ .	ϕ .	μ .	
1872 Jan. 0.0	$-97^\circ 26'$	$208^\circ 12'$	$2^\circ 5' 3$	613.52	Peters
1875 Jan. 1.5	$-82 \quad 25$	$208 \quad 38$	$2 \quad 7 \cdot 8$	614.19	Stockwell
1876 Apr. 5.	$-80 \quad 3$	$208 \quad 53$	$2 \quad 8 \cdot 9$	614.12	"
1878 Sept. 2.	$-79 \quad 11$	$205 \quad 49$	$2 \quad 15 \cdot 8$	614.74	"
1879 Nov. 16.	$-78 \quad 4$	$204 \quad 53$	$2 \quad 19 \cdot 1$	615.72	"
1880 Dec. 20.	$-76 \quad 27$	$204 \quad 28$	$2 \quad 19 \cdot 7$	615.57	"
1883 July 12.	$-72 \quad 58$	$203 \quad 46$	$2 \quad 22 \cdot 5$	614.74	"
1884 Sept. 24.	$-74 \quad 46$	$200 \quad 40$	$2 \quad 28 \cdot 5$	614.40	Oppenheim
1885 Dec. 8.	$-72 \quad 39$	$200 \quad 52$	$2 \quad 30 \cdot 0$	614.82	Tietzen
1887 Feb. 21.	$-70 \quad 5$	$201 \quad 11$	$2 \quad 30 \cdot 9$	615.03	"
1888 May 6.	$-68 \quad 36$	$200 \quad 45$	$2 \quad 35 \cdot 0$	613.90	"
1889 July 20.	$-68 \quad 51$	$198 \quad 49$	$2 \quad 40 \cdot 9$	614.24	Lange
1890 Oct. 3.	$-68 \quad 26$	$197 \quad 13$	$2 \quad 44 \cdot 0$	615.66	"
1894 May 15.	$-63 \quad 34$	$195 \quad 54$	$2 \quad 46 \cdot 7$	614.72	"
1895 July 29.	$-61 \quad 26$	$195 \quad 53$	$2 \quad 47 \cdot 7$	614.77	"
1896 Oct. 11.	$-59 \quad 14$	$196 \quad 10$	$2 \quad 46 \cdot 4$	615.15	"
1897 Dec. 25.	$-56 \quad 44$	$196 \quad 37$	$2 \quad 45 \cdot 8$	615.62	"
1899 Mar. 10.	$-55 \quad 21$	$195 \quad 54$	$2 \quad 52 \cdot 4$	615.11	"
1901 Aug. 7.	$-54 \quad 59$	$192 \quad 34$	$2 \quad 59 \cdot 9$	615.80	"
1904 Jan. 4.	$-51 \quad 54$	$191 \quad 30$	$3 \quad 0 \cdot 4$	615.60	"
1905 Apr. 28.	$-49 \quad 48$	$191 \quad 7$	$3 \quad 1 \cdot 5$	615.07	"
1907 Sept. 25.	$-45 \quad 50$	$189 \quad 41$	$3 \quad 3 \cdot 8$	615.37	"
1908 Oct. 29.	$-44 \quad 19$	$190 \quad 46$	$3 \quad 5 \cdot 4$	615.77	"
1911 May 7.	$-40 \quad 56$	$189 \quad 54$	$3 \quad 11 \cdot 2$	614.37	"

17. The changes in the elements here are visibly systematic, the slight variations from the systematic being in all cases traceable to the different computers. They are, therefore, approximately correct. Yet if we calculate from those of 1875 we shall find that then the action was not libratory, while now we should conclude it to be so, and it will clearly not be so again a few years hence. Thus for 1875 we find

$$\frac{d\theta}{dt} = 14.5, \quad \sqrt{A} \cos \frac{1}{2}(\theta - \gamma) = 9.2,$$

that is

$$\frac{d\theta}{dt} > \sqrt{A} \cos \frac{1}{2}(\theta - \gamma).$$

Thus the action was not libratory in 1875.

18. Since the old criterion fails we must seek another. At the limit of libration

$$\pm \frac{d\theta}{dt} = \pm \sqrt{\frac{1}{2}A} [\cos(\theta - \gamma) - \cos\beta],$$

whence

$$\theta - \gamma = \beta \quad \text{or} \quad \theta = \beta + \gamma.$$

If $\beta + \gamma$ is over 90° , $\cos \theta$ has a $-$ sign and the left side

$$n - 2n' + \frac{d\varpi}{dt} + \frac{d\epsilon}{dt},$$

cannot be 0 for positive values of $n - 2n'$, since

$$\frac{d\varpi}{dt} = -c \cos \theta,$$

c being the whole coefficient. Permanent libration is thus impossible for

$$\beta > 90^\circ - \gamma.$$

If $n - 2n'$ be negative, $\cos \theta$ must be negative; the libration takes place round 180° and $\theta > 90^\circ$,

$$\beta > 90^\circ - \gamma.$$

For

$$\frac{d\theta}{dt} = \sqrt{\frac{1}{2}A} [-\cos(\theta - \gamma) - \cos\beta].$$

$$\beta > 270^\circ - \gamma.$$

The criterion, therefore, for the gap $n=2n'$ is

$$n-2n'=e \cos \theta,$$

where

$$e = \frac{n\alpha m'}{2e} (4 b^{(2)} + b_1^{(2)}).$$

Taking the maximum possible value of $\cos \theta=1$, we get

$$(11) \quad n-2n' < \frac{n\alpha m'}{2e} (4 b^{(2)} + b_1^{(2)}).$$

19. Applying this criterion we find that not a single asteroid in the gap $n=2n'$ shows libration. The gap, therefore, is not due to that cause, but is permanent, and expresses a secular action by Jupiter, which has cleared the gap and keeps it so.

20. For the gap $n=3n'$

$$\begin{aligned} \frac{dR}{de} = \frac{1}{8} n^2 a^2 \alpha m' \left\{ 2e (21 b^{(3)} + 10 b_1^{(3)} + b_2^{(3)}) \cos \theta \right. \\ \left. - e' (40 b^{(2)} + 20 b_1^{(2)} + 2 b_2^{(2)}) \cos \theta' \right\}, \end{aligned}$$

whence

$$\begin{aligned} \frac{d\varpi}{dt} = \frac{1}{8} n \alpha m' \left\{ 2 (21 b^{(3)} + 10 b_1^{(3)} + b_2^{(3)}) \cos \theta \right. \\ \left. - \frac{e'}{e} (40 b^{(2)} + 20 b_1^{(2)} + 2 b_2^{(2)}) \cos \theta' \right\}, \end{aligned}$$

the secular terms being as before.

Introducing this condition for $\textcircled{132}$, we see that the action on it too fails of being libratory.

21. This investigation shows, then, that the gaps considered are permanent and due to secular action by Jupiter, libratory action playing no part in their formation. The same can be seen from their position to be the case with the gaps in the rings of Saturn, and, finally, in the positions of the major planets, which I propose making the subject of a separate paper.

In conclusion, I wish to express my obligation to Miss E. S. Williams, of this observatory, for her valuable assistance.

Boston, Mass.,
August 10, 1911.

XXXI. *On the Effect of Clouds on Ionization.* By GWILYM OWEN, M.A., D.Sc., and JOSEPH H. T. ROBERTS, M.Sc., University of Liverpool*.

DURING some experiments on the electrical conductivity of air containing certain vapours, we noticed that the production of a cloud in the gas by an adiabatic expansion caused a marked diminution in the ionization current. It occurred to us that this expansion method of producing mists and clouds would afford a reliable means of investigating the effects of clouds of different densities upon the conductivity produced in a gas by a constant ionizing source.

In order satisfactorily to investigate the effect on the conductivity of a gas of the presence in it of foreign particles in suspension, it is essential that means be found

- (1) for producing repeatedly a set of particles of constant number and of uniform size ;
- (2) for varying the number and size of the particles at will.

These means are readily secured by using as suspended particles either the charged water-drops formed when moist ionized dust-free air is subjected to an adiabatic expansion of magnitude greater than 1·25, or the uncharged water-drops formed when ordinary moist dust-free air is subjected to an expansion greater than 1·38 †.

Now since it is impossible in practice to study the ionization current through the air at the instant of the formation of the cloud, it seems likely that both types of cloud (viz., those in ionized and those in normal air) will produce more or less similar effects. For if a cloud be uncharged initially, it will very soon contain under the action of the ionizing rays a fair proportion of charged drops of both signs, while the cloud which is charged to start with will very soon contain a certain proportion of uncharged drops. Hence a cloud obtained in this way, in addition to possessing the important advantages mentioned above, is quite representative of any set of suspended particles such as dust, smoke, mist, fog, &c., which have to be considered in their bearing upon the phenomena of atmospheric ionization.

Experimental arrangements.

A general idea of the final form of our apparatus is given by the figure. A represents the metal ionization-chamber connected as shown to a Wilson expansion apparatus. By connecting A to one terminal of a battery of small cells, the

* Communicated by the Authors.

† C. T. R. Wilson, Phil. Trans. clxxxix. p. 265 (1897).

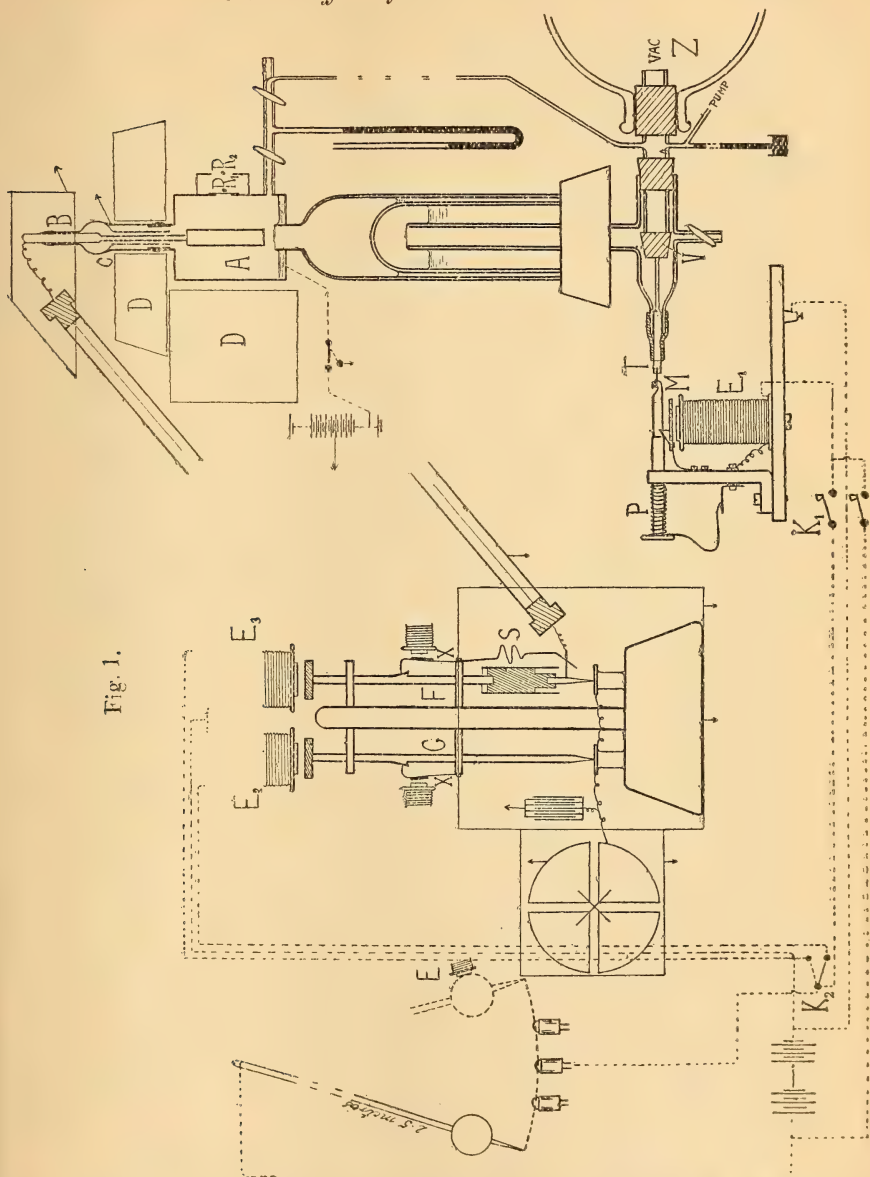


Fig. 1.

ions produced inside the chamber by the radium R_1 were driven to an insulated central electrode and thence through an earthing key and a cut-off key to a Dolezalek quadrant electrometer.

Phil. Mag. S. 6. Vol. 23. No. 135. March 1912. 2 B

The Ionization-Chamber.

The ionization- and cloud-chamber A consisted of a cylindrical brass tube about 8 cm. long and 5 cm. in diameter, furnished with two small glass windows through one of which entered a beam of light from a distant Nernst lamp, while through the other could be obtained a view of the cloud. The central electrode consisted of a piece of brass rod about 1 cm. diameter. On account of the repeated production of clouds in our experiments it was necessary to devise means to prevent the insulation of the electrode from being destroyed by the deposition of moisture; this was secured by supporting the electrode by means of sealing-wax from the upper end of a long narrow glass tube B, care being taken that the electrode did not touch the tube at any other point. The electrode was arranged vertically to reduce deposition to a minimum, and the lower end of the insulating glass tube was coated with sealing-wax. Direct leak from the charged tube to the electrometer was prevented by insulating the brass tube C from A, and connecting C to earth. Extraneous ionizing action of the radium was prevented by thick lead blocks D, the upper block being tunnelled to receive the tube C.

For an account of Wilson's expansion apparatus, reference must be made to Wilson's original paper (Proc. Camb. Phil. Soc., p. 333, 1897) or to J. J. Thomson's 'Conduction of Electricity through Gases,' page 154. The descent of the piston (and thus the expansion of the air in A) is brought about by opening the valve V, thus putting the lower side of the piston in communication with the exhausted chamber Z.

In our earlier experiments the valve V was opened by pulling the rod T by hand; since, however, the magnitude of the expansion depends upon the suddenness with which this is done, we found it necessary to arrange for the valve to be opened mechanically. As is shown on the diagram, the necessary force was supplied by the release of a powerful compressed spring P. Further, the pressure in the vacuum was always adjusted to a certain value before an expansion was made. In this way the magnitude of the expansion corresponding to any given pressure-drop was made very definite.

Since the cloud begins to fall immediately it is formed, it is desirable that the measurement of the ionization current be completed within as short an interval as possible after the expansion. On the other hand, when a cloud is formed on the ions, the air is temporarily robbed of its ions and a certain interval must elapse before the ionization once more attains

a steady state ; this interval, in fact, was very small in our experiments, certainly under one second. Nevertheless, we found it convenient (except where otherwise stated) to allow three seconds to elapse between the expansion and the unearthing of the quadrants. For the same reason it is also desirable to measure the ionization current through the cloud over as small an interval of time as possible. Here again we found three seconds to be a convenient and reasonable interval.

It is clear that the keys could not be manipulated by hand with the degree of exactness required when dealing with such short intervals ; accordingly, all three operations of firing off the expansion, unearthing the quadrants, and stopping the charging up were performed by electromagnets controlled by a single pendulum. The latter consisted of a massive iron block at the end of a brass tube 2.5 metres long.

Referring to the dotted lines in the diagram which indicate electrical connexions, it will be seen that when the key K_1 is depressed the pendulum P on its next passage through the mercury will actuate the electromagnet E_1 which fires off the expansion. If the key K_2 be depressed immediately before the next passage of the pendulum through the mercury in the same direction, the electromagnet E_2 will be actuated at the passage and the quadrants will be unearthed. In the same way, by putting K_2 over to the dotted position the magnet E_3 will be actuated at the next passage and the connexion between the ionization-chamber and the electrometer will be broken. Both keys on being pulled up are retained in position by small spring catches XX. Thus the time between the expansion and the unearthing, and that between the unearthing and cessation of the charging up, is one complete swing of the pendulum (about three seconds).

The keys F, G require brief mention. They consist essentially of pointed brass rods resting against brass plates supported on sealing-wax pillars. This arrangement was adopted in preference to the usual mercury-cup type, as we found the latter to give trouble on account of electrostatic and thermoelectric effects. The shaded part of key F is of ebonite enclosed as shown in a metal "umbrella," in order to overcome a difficulty which arose from the charging up of the ebonite in its very rapid passage through the air when pulled up by the electromagnet. Immediately after the key F broke contact with the brass plate it made contact with the earthed spring S, thus preventing inductive action on the electrometer system which would otherwise have resulted from the continuous charging up of the key F.

The keys F and G could be dropped by releasing the spring catches by the small electromagnets shown at the sides: thus the keys were never touched by hand, and consequently all operations could be reproduced identically. The electrometer and keys were enclosed in earthed metal boxes. These arrangements were found to work very satisfactorily; measurements of the ionization current in cloudless air concurred within considerably less than one half per cent. During the experiments the radium was used in one or other of two standard positions, R_1 and R_2 in fig. 1. The ionization inside A with radium in position R_1 was six times as intense as in position R_2 . It remains to add that during any one set of observations the air inside the apparatus was never changed, the clouds being removed by repeated small expansions.

Experiments.

With this apparatus we have investigated the following:—

- (1) The effects of clouds of constant density upon the ionization current under different intensities of electric field.
 - (2) The effects of clouds of various densities upon the current under a constant electric field.
 - (3) The manner in which the effect of a cloud upon a current varies with the age of the cloud.
- (1) *The effect of clouds of constant density upon the ionization current under different intensities of electric field.*

In Table I. the first column gives the potential on the ionization-chamber. The second column gives the current through cloudless air at a pressure of 58.3 cm. of mercury; for since the current depends upon the pressure, it is clear that, in order to compare the currents through cloudless and cloudy air, the current must in all cases be measured with the piston of the expansion apparatus in its lowest position, when the pressure in the ionization-chamber is less than atmospheric by an amount equal to the pressure-drop for this expansion. Column 3 gives the current through a cloud formed on the ions produced by the γ rays from the radium, and caught by an expansion of 1.32. It must be noted, however, that there was no electric field on when the expansions were made; otherwise, since various fields were applied, the clouds produced upon the ions would not have been of constant density, owing to the different numbers of

ions present in the steady state under the various fields. This deletion of the ions by the electric field is clearly shown by the numbers in column 4, which gives the current through the clouds obtained by expanding with the field on; it will be noticed that the effects of the clouds obtained under these conditions are distinctly smaller than the effects of the clouds obtained when the field is off at the moment of expansion. (In fact, in so far as the retarding effect of a cloud produced by a given expansion is a measure of the number of ions caught, a comparison of columns 3 and 4 gives an idea of the number of ions present in the steady state under different potentials with a given intensity of ionization.)

TABLE I.

Radium in position R_1 (strong ionization). See figure.

Expansion 1.32.

Character of cloud—very dense. Time to fall through 5 cm. = 90 secs. (approx.).

Interval between expansion and unearthing, 3 secs.

Time of charging up, 3 secs.

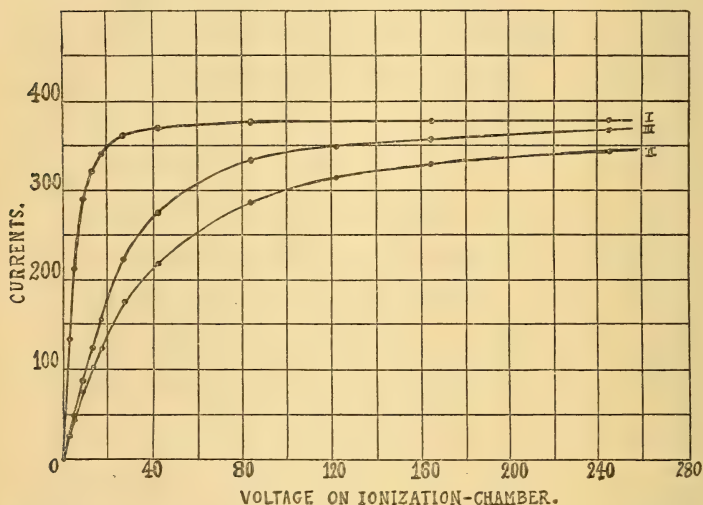
The letters *a, b, c, d*, attached to the numbers in the first set indicate the order in which the observations in each set were made.

Volts on ionization chamber.	Current. No cloud.		Current through cloud. No field on when expansion was made.	Current through cloud. Field on when expansion was made.
— 2	(a) 132.0	(c) 132.0	(b) 27.5	(d) 28.5
— 4.5	212.0	212.0	44.0	49.0
— 8.5	290.5	290.0	75.0	87.5
— 13.0	323.0	323.0	102.5	122.5
— 17.0	341.0	341.0	122.5	155.5
— 27.0	361.5	361.5	176.5	222.0
— 42.0	370.0	370.0	219.5	276.5
— 84.0	377.0	377.0	287.0	335.0
— 122.0	379.0	378.5	313.5	349.5
— 164.0	378.5	378.5	330.0	359.5
— 245.0	379.5	379.5	342.0	367.5

These results are shown graphically in fig. 2. Curve I. gives the currents through cloudless air. Curve II. gives the currents through the clouds of constant density obtained on expansion with no field on; the field was put on immediately after the expansion so that the steady state was attained well before the quadrants were unearthed. Comparison of

Curves I. and II. shows clearly that the effect of the cloud diminishes with increasing fields, i. e., with increasing ionic velocities; thus the diminution of the current by the cloud is 79 per cent under 2 volts, and only 10 per cent under 240 volts. Curve III., lying all the way above Curve II., gives the currents through the clouds obtained on expansion with the field on.

Fig. 2.



It will be convenient at this stage to discuss the cause of this marked diminution of the ionization current by the cloud.

The effect upon ionization of foreign particles in the gas was first observed by R. B. Owens*, who found that introducing tobacco smoke into the ionized air greatly reduced the ionization current. More recently A. S. Eve† has studied, by means of an Ebert instrument, the effect of dust and smoke upon the ionization produced in air by the γ rays of radium. J. J. Thomson‡ explains the effect of dust or smoke as follows:—"The effect produced by dust is easily explained, as the dust particles are in all probability very large compared with the ions; thus if a positive ion strikes against a dust particle and sticks to it, it forms a large system which is much more likely to be struck by a negative ion and neutralized than if the positive ion had

* Phil. Mag. Oct. 1899.

† Phil. Mag. May 1910.

‡ 'Conduction of Electricity through Gases,' p. 20.

remained free ; in this way the presence of dust will facilitate the recombination of the ions."

On this view, therefore, the number of free ions present at any instant in dusty or smoky air is less than in clear air. Eve, on the other hand, suggests a different explanation, namely, that the presence of dust, smoke, and other centres, charged or uncharged, in the air causes a transformation from small mobile ions to large ions of very low mobility. In this way "the total number of ions present may be increased while the conductivity may be decreased." Eve's explanation is supported by the fact that the ionization current in his experiment was found to be *increased* by the presence of smoke under strong electric fields (3000 volts per cm.), whereas the smoke *decreased* the current under moderate fields (600 volts per cm.).

In our experiments, however, the maximum electric force was only about 120 volts per cm. and was, therefore, far too small to move appreciably in 3 seconds the cloud-particles even if they were multiply-charged. Thus the currents through the clouds must have been carried by small unloaded ions, and consequently the diminution of the current by the cloud must be due partly to the water-drops acting as mechanical obstacles to the motion of the ions and partly to the more rapid recombination of the ions or to their replacement by large ions of small mobility. The potential at our disposal was too small to enable us to decide between these two alternatives.

II. *The effects of clouds of various densities upon the current under a constant electric field.*

Clouds of various densities can be readily obtained by three different methods :—

- (a) by subjecting air under the action of a constant ionizing source to expansions of different magnitudes;
- (b) by subjecting normal air to expansions of different magnitudes, in which case we are dealing with Wilson's "rain-like condensation" or "cloudy condensation" according to the magnitude of the expansion ;
- (c) by subjecting air to a constant expansion under ionizing rays of different intensities.

In our present experiments we have adopted methods (a) and (b) only, reserving (c) for future investigation.

The results obtained according to method (a) are shown in Tables II. and III.

TABLE II.

Volts on Tube -22.

Radium in position R_2 , see fig. (weak ionization).

Expansion $\frac{V_2}{V_1}$.	Current before expansion. C_1 .	Current after expansion. C_2 .	Observation.	$\frac{C_2}{C_1} \times 100$.
1.233	...	...	Few drops.	...
1.245	418	400	Fair shower.	95.7
1.250	412	380	Dense shower.	92.2
1.262	410	349	Cloud.	85.1
1.280	402	302	"	75.1
1.295	396	292	"	73.7
1.308	392	288	"	73.5
1.322	391	279	"	71.4
1.334	387	277	"	71.6
1.349	386	272	"	70.5
1.374	379	265	"	69.9
1.395	375	251	"	66.9
1.438	362	208	"	57.5

TABLE III.

Volts on Tube -4.

Radium in position R_2 (weak ionization).

Expansion $\frac{V_2}{V_1}$.	Current before expansion. C_1 .	Current after expansion. C_2 .	Observation.	$\frac{C_2}{C_1} \times 100$.
1.222	...	...	No effect.	...
1.230	420.5	416.5	Thin shower.	99.1
1.236	416.0	392.0	Fair shower.	93.7
1.243	415	272.0	Very dense shower.	65.6
1.253	410	207	Thin cloud.	50.5
1.264	410	130	Heavy cloud.	31.7
1.273	409	114	"	27.9
1.281	406	111	"	27.3
1.288	405	108	"	26.7
1.299	404	105	"	26.2
1.307	403	104	"	26.0
1.320	401	99	"	24.7
1.355	393	93	"	23.7
1.372	390	90	"	23.1
1.401	383	84	"	21.9
1.436	375	75	"	20.0

The results of Tables II. and III. are shown respectively in Curves I., II., fig. 3 (Curve III. will receive mention later). Curves I. and II. were obtained under identical conditions, except as regards potential—the voltage on the

tube being -22 for Curve I. and -4 for Curve II. It is interesting to note the striking difference between the two curves.

A closer inspection of the curves shows that the results of the expansions present interesting features at expansions of magnitudes 1.25 , 1.28 , 1.31 , and 1.38 . Now these are the identical values of the expansions which C. T. R. Wilson found

- (a) to start catching the negative ions,
- (b) to catch all the negative ions,
- (c) to start catching positive ions,
- (d) to catch the nuclei of cloudy condensation.

The most remarkable feature, however, is that whereas the cloud formed on the negative ions under a potential of 22 volts diminishes the current by 26 per cent., and under 4 volts by 74 per cent., yet the supposed increase in the number of cloud particles when the positive ions are caught at an expansion of 1.31 produces a further decrease of only some 3 per cent. This result may be due to either of the following causes:—

(a) the number of positive ions caught is, owing to the greater efficiency of the negative ions, enormously less than the number of negative ions caught when both are present in the same space, and when the expansion is known to be big enough to catch both kinds of ions, or

(b) when the density of a cloud exceeds a certain value a further moderate increase in the density produces very little further diminution of the ionization current through the gas.

There is no doubt that cause (a) may come in as J. J. Thomson found in determining the ionic charge*, unless care be taken to make the expansion extremely rapid.

Since in our experiments the expansion was very rapid, and since, in addition, the further diminution in the current due to the positive ions at their maximum effect (expansion 1.36) is only some 3 per cent., we incline to the second of the two explanations. It may be noticed, however, that under a voltage of -22 the increase in the density of the cloud at 1.38 due to the catching of the nuclei of cloudy condensation is well marked, whereas it is almost inappreciable under -4 volts, when the current had already suffered the large reduction of nearly 80 per cent. before these nuclei started to come in. Thus the greater the percentage reduction of the current already produced by the cloud, the

* 'Conduction of Electricity through Gases,' 2nd ed. pp. 157, 158 (1906).

less the further reduction due to a marked increase in the number of cloud particles.

Table IV. gives the results of observations made on the current under a potential of -16 volts through the showers and clouds obtained in *normal air* at different expansions.

TABLE IV.

Volts on Tube -16 .

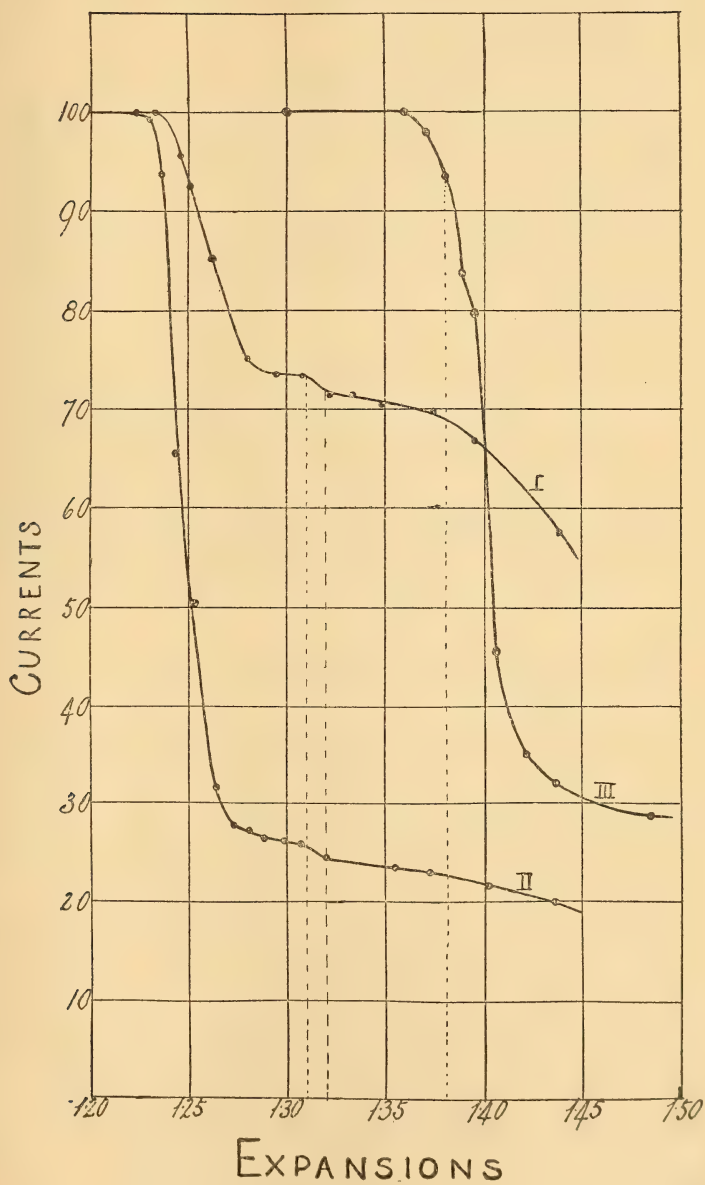
Radium absent when expansion was made, and then immediately placed in position R_1 (strong ionization).

Expansion $\frac{V_2}{V_1}$.	Current before expansion. C_1 .	Current after expansion. C_2 .	Observation.	$\frac{C_2}{C_1} \times 100$.
1.300	248	248	Few drops.	100
1.360	239	238.5	Thin shower.	100
1.370	238.5	233	Heavy shower.	97.9
1.380	236.5	220	Very dense shower.	93.3
1.388	235	196	Cloud.	83.4
1.395	234	187	Dense cloud.	79.9
1.406	233	166	Fog.	45.5
1.420	231	81	"	35.0
1.436	228	73	"	32.0
1.485	226	65	"	28.8

In these experiments the radium was hidden behind a thick lead screen when the expansion was made, and was brought into position R_1 immediately afterwards. The interval between the expansion and the unearthing was still 3 seconds, but after some practice it was found that the radium could be brought into the required position well before the 3 seconds were up. The numbers in the last column are shown plotted against the expansions in Curve III., fig. 3. From this it is seen that a "shower" has very little effect upon the current, consequently the curve only begins to drop at an expansion of about 1.37. At an expansion of 1.385, however, there is a decided increase in the slope of the curve; this is of course where the cloudy condensation commences. The sudden increase in the density of the cloud now produces a very large reduction in the current, but as is seen from the curve this reduction does not proceed indefinitely, attaining rather a saturation value at an expansion of about 1.45.

Again, the marked diminution in the current at an expansion of 1.38, and also an inspection of the cloud itself, suggested that the cloud obtained at an expansion greater

Fig. 3.



than 1.38 was *more dense* when the radium was absent than when the radium was in position. This point was tested with the following results :—

Expansion 1.436.

Current before expansion 230.0.

Current through cloud obtained with radium in position R_1 when expansion was made, 100.0.

Current through cloud, radium being absent when expansion was made, 73.5.

The above numbers prove conclusively that far fewer nuclei of cloudy condensation come into action when the gas is subjected to strong ionizing rays. This effect may be due to two causes :—

- (a) the ions, owing to their greater efficiency as condensation nuclei, monopolize the water vapour, and, therefore, the drops formed round the nuclei of cloudy condensation do not attain the critical equilibrium size.
- (b) the ionizing rays may, in some way, prevent the accidental agglomeration of water molecules, to which the nuclei of cloudy condensation are attributed, *e. g.*, by increasing the rapidity of their coalescence to form fewer but larger drops.

III. *The manner in which the effect of a cloud upon the current varies with the age of the cloud.*

We thought it would be interesting to see if any marked change takes place in the cloud in the earlier stages after its production. These changes might possibly be detected by measuring the ionization current through the cloud at different times after its production. To detect any possible interesting features, however, it is necessary that the ionization current be measured over a very small interval of time, say a fraction of a second, otherwise transitory effects would be lost. To carry this out we arranged for the long pendulum to swing through two mercury cups, some 17 cm. apart, the total amplitude of the pendulum being about twice that amount. The amplitude of the pendulum was kept constant by releasing the iron bob from a fixed deflected position, in which it had been held by an electromagnet; thus the time taken by the pendulum to pass from one mercury cup to the other in its first swing was constant, and equal to 0.25 second. A metronome was arranged so that a wire attached the oscillating lever passed through a mercury cup at the

middle of its swing. On pressing a key just before this lever passed through the mercury a relay was worked at the next passage, and the expansion was fired. Just before the n th passage of the metronome lever through the mercury another key was depressed, and on the n th passage a second relay was actuated, which broke the current holding back the pendulum. The latter then swung forward through the two mercury cups; on passing through the first it actuated electromagnet E_1 , thus unearthing the quadrants, and on passing through the second it actuated E_2 , thus stopping the charging up. It will be seen, from the numbers in Table V., that although the time of charging up was so short, the duplicated observations are in very good agreement.

TABLE V.

Potential on ionization-chamber -20 volts.

Radium in position R_1 (strong ionization).

Constant value of the expansion $\frac{V_2}{V_1} = 1.331$.

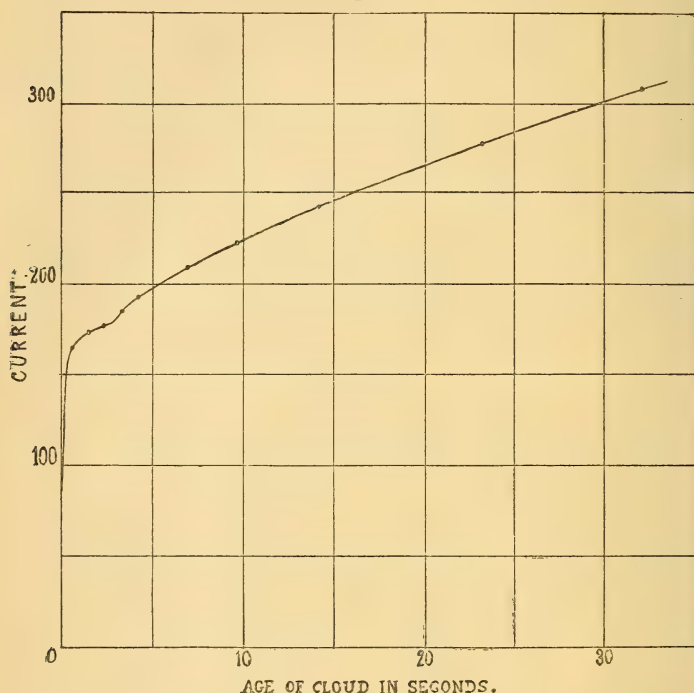
Constant time of charging up of electrometer $= 0.25$ second.

The letters a, b, c, d , represent the order in which the readings were taken.

Current before expansion.		Current through cloud.		Time between expansion and unearthing electrometer $= x + nt$ where $x = 0.6$ sec. and $t = 0.9$ sec.
(a) 382.5	(c) 383.0	(b) 165.0	(d) 166.0	x
382.5	382.0	173.0	171.5	$x + t$
382.5	382.0	177.0	176.0	$x + 2t$
382.0	382.5	185.5	187.0	$x + 3t$
382.5	382.5	196.0	192.5	$x + 4t$
382.0	383.0	198.5	198.0	$x + 5t$
383.0	383.0	208.5	208.5	$x + 7t$
383.0	383.0	225.0	223.0	$x + 10t$
382.5	382.0	242.0	246.0	$x + 15t$
383.5	383.0	277.0	277.0	$x + 25t$
383.0	383.5	316.0	302.0	$x + 35t$

The mean numbers given in Table V. are shown graphically in fig. 4. When the age of the cloud is greater than about 4 seconds the curve shows no interesting features, the current simply increasing owing to the evaporation and settling of the cloud and regaining its normal value in about 90 secs.; an inspection of the ionization-chamber after that time showed that the cloud had all disappeared.

Fig. 4.



Before the age of 4 seconds, however, the curve exhibits certain irregularities, which are probably the joint effect of the following processes going on in the ionization-chamber immediately after the formation of the cloud:—

- (a) Rapid replacement of the ions caught by the cloud.
- (b) Partial diselectrification of the charged cloud by the action of the ionizing rays.
- (c) Thinning of the cloud by the evaporation of drops too small to be in equilibrium.
- (d) Settling of the cloud.

Now the curve shows that in 0·6 of a second the current rises to within a few per cent. of, say, a 5 second cloud value. Since an expansion of 1·331 catches practically all the ions, it is evident that the replacement of the ions occurs very rapidly. Since, further, the settling of the dense cloud takes place only very slowly, we must regard the shape of the curve for the cloud at ages between 1 and 3 seconds as being mainly due to a combination of (b) and (c) above. We propose testing this point further, varying the conditions as regards intensity of ionization and density of cloud.

Summary.

(1) The problem investigated is the effect of suspended particles upon the ionization current in air, the ionizing agent being the γ rays of radium.

(2) As suspended particles the writers have utilized the cloud particles formed when moist ionized dust-free air is subjected to an adiabatic expansion.

(3) This method, so far as we know, is the only method (applicable to the problem) of producing repeatedly a set of minute particles of constant number and of uniform size, the number and size being readily controllable.

(4) The ionization current in cloud-laden air is smaller than the current in cloudless air, the extent of the reduction depending upon

(a) the intensity of the electric field, *i. e.* the ionic velocities;

(b) the density of the cloud.

A cloud falling at the rate of 1 cm. in 20 seconds diminished the ionization current under an electric force of 2 volts per cm. by 75 per cent., and that under an electric force of 120 volts per cm. by 10 per cent.

(5) The denser the cloud the greater is the percentage diminution in the current, but when the percentage diminution reaches a certain value, of the order of about 75 per cent., any further increase in the density of the cloud does not result in any further reduction in the ionization current.

(6) For this reason a cloud produced on equal numbers of positive and negative ions has very little greater retarding effect upon the current than the cloud produced on the negative ions alone.

(7) The number of nuclei of Wilson's foggy condensation caught by an expansion greater than 1.38 is greatly reduced by the presence of ions in the gas.

(8) An investigation of the manner in which the effect of a cloud upon the current varies with the age of the cloud indicates that in the early stages after its formation a cloud exposed to ionizing rays undergoes certain rapid changes.

(9) Incidentally the experiments illustrate in a new way the results obtained by C. T. R. Wilson, *viz.*: the catching of the negative ions at an expansion of 1.25, positive ions at 1.31, and production of cloudy condensation in unionized air at an expansion of 1.38.

In conclusion we wish to express our thanks to Professor Wilberforce for many valuable suggestions during the progress of this work.

Holt Physics Laboratory,
University of Liverpool.

XXXII. *On the Instability of Gaseous Jets.* By JOSEPH H. T. ROBERTS, *M.Sc.*, and E. MEIGH, *M.Sc.*, *University of Liverpool* *.

AS a result of some experiments on the flow of gases through tubes, the writers were led to consider how the phenomena of flow would be modified as the tubes were made shorter and shorter, until they ultimately approximated to holes in infinitely thin plates. It is well known that if the pressure causing a gas to flow through an orifice into an atmosphere be increased beyond a certain critical value the flow becomes irregular, and also that under certain circumstances the gaseous jet may exhibit a sensitiveness to sonorous vibrations, a familiar example of such sensitiveness being that of the sensitive gas-flame. Most experimenters upon sensitive flames appear to have used the pin-hole steatite burner, or a drawn-out glass tube, but there is reason to believe that greater sensitiveness can in general be obtained with jets from holes in very thin plates, and these jets are more immune from the influence of disturbances other than sonorous vibrations.

The instability or sensitiveness of a jet depends upon the vorticity. Before proceeding to describe experiments upon jets, it will be well to discuss the theory †, and to see what *a priori* reason there is to expect that the jet from a tube will, in general, be more stable than one from a hole in a thin plate.

“In the ideal case of abrupt transitions of velocity, constituting vortex sheets, in frictionless fluid, the motion is always unstable, and the degree of instability increases as the wavelength of the disturbance diminishes.

“The direct application of this result to actual jets would lead us to the conclusion that their sensitiveness increases indefinitely with pitch. It is true that, in the case of certain flames, the pitch of the most efficient sounds is very high, not far from the upper limit of human hearing; but there are other kinds of sensitive jets on which these high sounds are without effect, and which require for their excitation a moderate, or even a grave pitch.

“A probable explanation of the discrepancy readily suggests itself. The calculations are founded upon the supposition that the changes of velocity are discontinuous—a supposition that cannot possibly agree with reality. In consequence of fluid friction, a surface of discontinuity, even if it could ever

* Communicated by the Authors.

† Rayleigh, ‘Sound,’ vol. ii. ch. xxi.

be formed, would instantaneously disappear, the transition from the one velocity to the other becoming more and more gradual, until the layer of transition attained a sensible width. When this width is comparable with the wave-length of a sinuous disturbance, the solution for an abrupt transition ceases to be applicable, and we have no reason for supposing that the instability would increase for much shorter wave-lengths.

"There is, therefore, ample foundation for the suspicion that the phenomena of sensitive jets may be greatly influenced by fluid friction, and deviate materially from the results of calculations based upon the supposition of discontinuous changes of velocity. Under these circumstances it becomes important to investigate the character of the equilibrium of stratified motion.

"The manner in which viscosity operates is probably as follows. At the root of the jet, just after it issues from the nozzle, there is a near approach to discontinuous motion, and a high degree of instability. If a disturbance of sufficient intensity and of suitable period have access, the regular motion is lost, and cannot afterwards be recovered. But the instability has a very short time in which to produce its effect. Under the influence of viscosity the changes of velocity become more gradual, and the instability decreases rapidly, if it does not disappear altogether. Thus if the disturbance be insufficient to cause disintegration during the brief period of instability, the jet may behave very much as though it had not been disturbed at all, and may reach the full development observed in long flames and smoke-jets."

It would thus appear that in general, an orifice of tubular form would tend to increase the discrepancy between theory and practice, by communicating to the jet a stratified formation, and thus lowering the pitch of the disturbances to which it was sensitive, or reducing the sensitiveness altogether, while a thin-plate orifice might be expected to give, near the root of the jet, an approximation to discontinuous changes of velocity, and consequently a considerable degree of sensitiveness for disturbances of high pitch.

The apparatus used in these experiments consisted of weighted gas-bags; a special gas-meter reading 1 cu. ft. per rev., the dial being divided into 100 parts; a water-manometer attached about 2 inches below the orifice; and a number of orifices consisting of holes in thin circular plates of copper and platinum, the plates being secured in an annular screw-head holder, and of tubes, and holes in thick plates.

The greatest difficulty met with in these experiments is that the pressure necessary to produce flaring, or to bring a jet to its condition of maximum sensitiveness, is very much influenced by accidental irregularities in the orifice. Two orifices, identical in dimensions and method of manufacture, might be expected to give flames with identical properties, but this is far from being the case. So important are small irregularities in the rim, that an orifice which appeared perfect when viewed through a powerful microscope would produce variations of as much as 20 per cent. or 30 per cent. in, say, the flaring-pressures of the jets from its two surfaces. The quantities in the jet cannot be considered to be functions of the measurable dimensions of the orifice unless the jets from opposite surfaces are identical. We have never succeeded in securing the complete fulfilment of the latter condition, but the approximation depends upon the method of manufacturing the orifices. After trying a variety of ways, the method we found most successful was to grip the disk of metal (about 0.15 mm. thickness) between the convex cheeks of two curved pieces of hard brass strip, and to bore the hole with a lathe twist-drill through all three.

Various sources of sound were used to test the sensitiveness of the flames, including bird-calls, whistles, pipes, and vibrating bars. The sounds which affect these flames are all of very high pitch; as a general rule we found the sensitiveness to increase with the diameter of the orifice, but in the case of orifices above 2 mm. diam. the flames were very long and somewhat inconvenient. On one occasion, with an orifice 1.107 mm. diam., we obtained a flame which, without the aid of resonators, was practically as sensitive as the ear itself. It responded to a whistle at the opposite end of the building, and when the flame ceased to respond it was almost impossible to tell, by ear, whether the whistle was sounding or not.

Some results of observations on the jets from holes in thin plates are given in the following table; the minimum sensitiveness pressure is an arbitrary quantity, depending upon the pitch and intensity of the disturbing note.

It will be seen from the table that there is a considerable range of pressure over which the jet is sensitive, the development of sensitiveness with increase of pressure being very gradual. It should be mentioned that jets from very small holes in thin plates (about 0.3 mm. diam.) required about 80 cm. of water to make them flare, and did not exhibit any sensitiveness.

TABLE I.

Holes in thin plates. Thickness of plates 0.15 mm.

Diam. of Orifice in mm.	Mean pressure in cm. of water required for			Mean length (cm.) of flame when		
	Flaring.	Maximum Sensitive- ness.	Minimum Sensitive- ness.	Flaring.	Max. Sens.	Min. Sens.
0.619	31.3	30.6	16.0	19.5	21.0	13.8
0.643	39.0	36.0	19.0	20.5	23.5	17.5
0.719	36.5	32.0	18.0	22.0	25.0	19.0
0.905	36.0	33.0	17.5	37.0	41.0	29.0
1.107	34.0	33.0	23.0	38.0	52.0	42.0
1.30	12.6	11.6	6.0	38.5	54.0	37.0
2.0	10.0	9.0	4.0	35.0	60.0	45.0
3.0	5.0	4.0	2.7	50.0	65.0	60.0

Experiments were then made with jets from narrow glass tubes ; a number of observations are given in the following table. It will be seen that the range of pressure for sensitiveness is extremely small, in some cases the numbers in columns 4 and 6 being the same. A remarkable feature of the jets from tubes is the extreme suddenness of the transition from a condition of stability to one of flaring ; in some cases the slightest touch with the finger upon a large gas-bag would be sufficient to bring the flame from the one condition to the other.

In place of short tubes, in which the irregularity of the ends would probably have produced considerable effect, we used thick-plate orifices, and it is interesting to observe, in Table II. (p. 372), that as the diameter increases, that is as the length becomes less important, the sensitiveness begins to show itself. The flaring-pressure for a constant diameter decreases with the length in the case of every tube in Table II., but it increases with the thick-plate orifices. (Compare the following, Table II. tube no. 3, thick-plate no. 2, Table I. orifice no. 5.)

It thus appears that any tubularity of the orifice from which the jet issues, in general lowers the flaring-pressure and diminishes the sensitiveness for notes of high pitch ;

while the flames from holes in very thin plates combine great sensitiveness to sonorous vibrations of high pitch with considerable immunity from the influence of disturbances of other kinds.

TABLE II.

Diam. of tube in mm.	Length (cm.)	Flaring Press. in cm. of water.	Maximum Sensitive-ness Press. (cm. of water).	Degree of Sensitiveness.	Pressure at which Sensitiveness disappears.
0.7238	6.25	62.0			
	3.6	34.0			
	2.4	32.0			
	1.4	20.0			
0.9811	6.9	27.0			
	4.6	20.0			
	2.5	12.0			
1.133	9.75	21.0			
	5.55	16.0	16	Minute.	16
	3.2	9.0			
	1.6	7.0	7	Minute.	7
1.666	0.9	4.0			
	5.85	6.6	6.5	Slight.	5.5
	3.55	5.0	4.95	"	4.90
	2.8	5.0	4.95	"	4.80
2.381	1.6	3.6	3.6	"	3.6
	5.1	2.2	2.0	Slight.	2.0
	3.92	2.0	2.0	Moderate.	2.0
	2.23	1.4	1.4	"	1.4
1.054	1.33	1.0			
	Thick plate				
	0.629	9.4	9.0	Considerable.	8.7
1.140	Thick plate				
	0.313	10.4	10.0	Considerable.	9.4

In Table I. it will be noticed that the flaring-pressures for the first five orifices are not greatly different, but that there is a drop in the flaring-pressure when the diameter becomes greater than, say, 1.2 mm. This would seem to indicate that over a certain range of diameters of orifice the flaring depends simply on what might be called the linear velocity of flow at the orifice. With a view to testing this point we

made a number of determinations of volumetric rates of flow, through the gas-meter. In Table III. are given the diameters, flaring-pressures, and volumetric rates of flow; the

TABLE III.

Diam. of Orifice in mm.	Flaring Press. in cm. water.	Amount passed per sec. when flaring, in cubic inches.	Linear Velocity of Flow × Constant.
0·619	31·0	1·152	3006
0·643	37·6	1·271	3073
1·100	37·0	3·756	3103
1·107	35·4	3·526	2914
1·30	13·4	2·879	1704
2·00	9·8	5·759	1440
3·00	5·8	10·06	1129

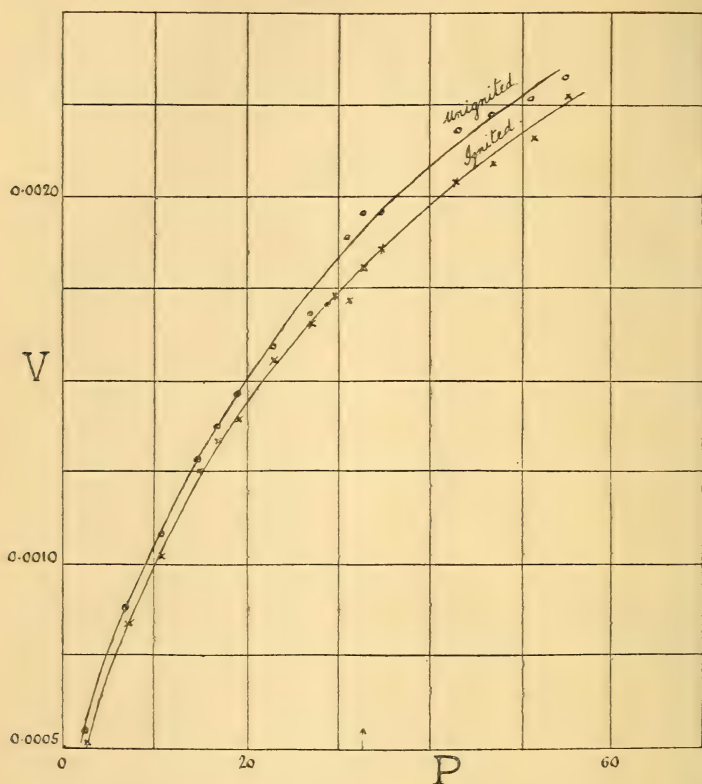
quantity in the last column, called linear velocity, is obtained by dividing the volumetric rate of flow by the square of the diameter of the orifice.

It is seen that the numbers in the last column show the same sudden drop as the flaring-pressures in Table I.

We have also made observations on the relation between pressure and rate of flow, with a given orifice, for ignited and unignited jets, and have found in every case that the rate of flow for a given pressure is greater for an unignited than for an ignited jet. "When a flame is lighted at the burner there are further complications, of which it is difficult to give an adequate explanation. The high temperature leads indeed to increased viscosity, and this tends to explain the higher pressures then admissible, and the graver notes which then become operative. But it is probable that the change due to ignition is of a still more fundamental nature" *.

The figure shows how the curve for the ignited jet lies below that for the unignited jet. P is the pressure in cm. of water and V is the volumetric rate of flow in cubic feet per second.

* Rayleigh, 'Sound,' vol. ii. p. 409.



In the upper curve there is great irregularity in the neighbourhood of the flaring-pressure; this appeared in all the curves. The flaring-pressure is shown by the arrow in the curve.

Conclusion.

The instability of a jet depends upon the vorticity at its surface. Any tubularity of the orifice from which the jet issues communicates stratified formation to the jet, and thus, in general, lowers the pitch of the sonorous disturbances to which it is sensitive, and diminishes the sensitiveness. The flaring-pressures of the flames from holes in thin plates are very much higher than those of the flames from tubes; on this account the flames from the former orifices are long and stiff. The transition of velocity at the surface of such jets is sudden, the pitch of the sonorous disturbances to which the jets are sensitive is very high, and the sensitiveness is

much greater than that of the jets from other orifices; in some cases the sensitiveness of a simple flame jet would approximate to that of the ear itself.

The flaring appears to depend, for a certain range of diameters of orifices, almost simply upon the linear rate of flow at the orifice. For diameters above this range, flaring occurs at much lower pressures.

The high temperature in ignited jets leads to increased viscosity, and this tends to explain the higher pressures then admissible. For a given pressure and orifice, the rate of flow is greater for an unignited than for an ignited jet.

In conclusion we wish to thank Professor Wilberforce for the keen interest which he has shown in these experiments.

George Holt Physics Laboratory,
University of Liverpool.

XXXIII. *Non-Newtonian Mechanics, The Mass of a Moving Body.* By RICHARD C. TOLMAN, Ph.D., Assistant Professor of Physical Chemistry at the University of Cincinnati*.

AN acceptance of the Einstein theory of relativity necessitates a revision of the Newtonian system of mechanics. In making such a revision it is desirable to retain as many as possible of the simpler principles of Newtonian mechanics. Some of the consequences have already been presented † of a system of mechanics which retains the conservation laws of mass, energy, and momentum, and defines force as the rate of increase of momentum; but to agree with the theory of relativity introduces an idea foreign to Newtonian mechanics by considering that both the mass and velocity of a body are variable.

From the theory of relativity, Einstein has calculated both the transverse and the longitudinal accelerations experienced by a charged body moving in an electromagnetic field. On the basis of these accelerations, it has been usual to place the "transverse mass" of a body moving with the velocity u as equal to $m_0 / \sqrt{1-u^2/c^2}$, and its "longitudinal" mass as equal to $m_0 / (1-u^2/c^2)^{3/2}$, where m_0 is the mass of the body at rest and c is the velocity of light. If, however, mass is a quantity to which a conservation law applies, the mass of a body cannot well be different in different directions; and

* Communicated by the Author. Contribution from the Chemical Laboratory of the University of Cincinnati.

† Lewis, Phil. Mag. xvi. p. 705 (1908). Lewis & Tolman, Phil. Mag. xvii. p. 510 (1909). Tolman, Phil. Mag. xxi. p. 296 (1911); xxii. p. 458 (1911).

it has been believed by Professor Lewis and the writer, that in general, without respect to direction, the expression $m_0/\sqrt{1-u^2/c^2}$ is best suited for THE mass of a moving body. They have already shown (*loc. cit.*), from the theory of relativity and the principles of non-Newtonian mechanics outlined above, that the consideration of a "transverse collision" between two moving bodies does lead to this expression for the mass of a moving body; and the purpose of the present article is to show that the consideration of any type of collision also leads to the same expression.

The immediate occasion of the present article is a recent attempt made by Mr. Norman Campbell* to show that the consideration of a "longitudinal collision" does not lead to the expression $m_0/\sqrt{1-u^2/c^2}$ for the mass of a moving body. There appears, however, to be an obvious error in his reasoning. Mr. Campbell wishes to find a relation between the mass of a body and its velocity and yet assumes that the mass of each of his bodies is the same after collision as before, although the velocities of course have changed (see equation (A) p. 627). Thus, although endeavouring to determine how the mass of a body depends on the velocity, he assumes in formulating his fundamental equation that it does not depend on the velocity at all†.

Longitudinal Collision.

Consider a system of Cartesian coordinates and two bodies moving in the X direction with the velocities $+u$ and $-u$ in such a way that a "longitudinal collision" will take place. Suppose the bodies are elastic and perfectly similar, each having the mass m_0 when at rest. On collision the bodies will evidently come gradually to rest, and then under the action of the elastic forces developed start up and move back on their original paths with the respective velocities $-u$ and $+u$ of the same magnitude as before.

Let us now consider how the collision will appear to an observer who is moving past the above system of coordinates with the velocity v in the X direction. Let u_1 and u_2 be the velocities of the two bodies as they appear before collision to this new observer. From Einstein's formulæ for the

* Phil. Mag. xxi. p. 626 (1911).

† In the same article, Mr. Campbell has also criticised the writer for referring the acceleration of a body under consideration to moving axes which have at the moment in question the same velocity as the body itself. As this is a procedure which has long been familiar to students of theoretical mechanics, has not in the past led to erroneous results, and in the cases under consideration leads to self-consistent conclusions, the writer cannot agree with Mr. Campbell's criticism.

composition of velocities we find for these velocities the relations $u_1 = \frac{u-v}{1-uv/c^2}$ and $u_2 = \frac{-u-v}{1+uv/c^2}$. Since these velocities are not of the same magnitude, the two bodies which have the same mass when at rest do not now have the same mass to this observer. Let us call these masses before collision m_1 and m_2 . During collision, the velocities of the bodies will all the time be changing; from the principle of the conservation of mass, however, the sum of the two masses will always equal $m_1 + m_2$ *. When in the course of the collision the bodies have come to relative rest and are both moving past our observer with the velocity $-v$, their momentum will be $-(m_1 + m_2)v$, and from the principle of the conservation of momentum this must be equal to the original momentum before collision, giving us the equation,—

$$-(m_1 + m_2)v = m_1 u_1 + m_2 u_2 = m_1 \frac{u-v}{1-\frac{uv}{c^2}} + m_2 \frac{-u-v}{1+\frac{uv}{c^2}}. \quad (1)$$

Simplifying, we have,—

$$\frac{m_1}{m_2} = \frac{1 - \frac{uv}{c^2}}{1 + \frac{uv}{c^2}}, \quad \dots \dots \dots (2)$$

which by direct algebraic transformations may be shown to be identical with

$$\frac{m_1}{m_2} = \frac{\sqrt{1 - \left(\frac{-u-v}{1+\frac{uv}{c^2}}\right)^2/c^2}}{\sqrt{1 - \left(\frac{u-v}{1-\frac{uv}{c^2}}\right)^2/c^2}} = \frac{\sqrt{1 - \frac{u_2^2}{c^2}}}{\sqrt{1 - \frac{u_1^2}{c^2}}}. \quad (3)$$

* In this connexion an interesting fact has been pointed out to the writer by Professor Lewis. As stated above, the sum of the two masses is throughout collision always equal to $m_1 + m_2$, and hence also at the time in the collision when the masses have come to relative rest their sum is $m_1 + m_2$. Since at this time both bodies are moving with the velocity $-v$ we might suppose that $m_1 + m_2$ equals $2m_0/\sqrt{1-v^2/c^2}$. This is not the case, however, since the bodies now possess additional elastic energy beyond that which they possess when at rest and not in contact. A relation between mass and energy has already been developed (*loc. cit.*), and the mass of this elastic energy must also be taken into account in calculating $m_1 + m_2$. In fact the consideration of a collision of this type leads to a simple proof of the relation between mass and energy, a proof presented by Professor Lewis in a series of lectures on the Theory of Relativity given at Harvard University in the Spring of 1911.

Remembering that these were bodies which had the same mass when at rest, we see that the mass of a body is inversely proportional to $\sqrt{1 - \frac{u^2}{c^2}}$, where u is its velocity, and have thus derived the desired relation,—

$$m = \frac{m_0}{\sqrt{1 - \frac{u^2}{c^2}}}.$$

Collision of Any Type.

A treatment of the general case of any type of collision between any two bodies elastic or otherwise is also possible, and leads to the same conclusion as to the desirability of using the expression $m_0 / \sqrt{1 - \frac{u^2}{c^2}}$ for the mass of a moving body.

For the mass m of a body moving with the velocity u let us write the equation $m = m_0 f(u^2)$ where $f(\)$ is the function whose form we wish to determine. The mass is written as a function of the square of the velocity, since from the homogeneity of space the mass will be independent of the direction of the velocity, and the mass is made proportional to the mass at rest since a moving body may evidently be divided into parts without change in mass.

Let us now consider two bodies having the masses m_0 and n_0 when at rest, moving with the velocities u and v before collision and with the velocities U and V after a collision has taken place.

From the principle of the conservation of mass we have,—

$$\begin{aligned} m_0 f(u_x^2 + u_y^2 + u_z^2) + n_0 f(v_x^2 + v_y^2 + v_z^2) \\ = m_0 f(U_x^2 + U_y^2 + U_z^2) + n_0 f(V_x^2 + V_y^2 + V_z^2), \end{aligned} \quad (1)$$

and from the principle of the conservation of momentum,

$$\begin{aligned} m_0 f(u_x^2 + u_y^2 + u_z^2) u_x + n_0 f(v_x^2 + v_y^2 + v_z^2) v_x \\ = m_0 f(U_x^2 + U_y^2 + U_z^2) U_x + n_0 f(V_x^2 + V_y^2 + V_z^2) V_x, \end{aligned} \quad (2)$$

$$\begin{aligned} m_0 f(u_x^2 + u_y^2 + u_z^2) u_y + n_0 f(v_x^2 + v_y^2 + v_z^2) v_y \\ = m_0 f(U_x^2 + U_y^2 + U_z^2) U_y + n_0 f(V_x^2 + V_y^2 + V_z^2) V_y, \end{aligned} \quad (3)$$

$$\begin{aligned} m_0 f(u_x^2 + u_y^2 + u_z^2) u_z + n_0 f(v_x^2 + v_y^2 + v_z^2) v_z \\ = m_0 f(U_x^2 + U_y^2 + U_z^2) U_z + n_0 f(V_x^2 + V_y^2 + V_z^2) V_z. \end{aligned} \quad (4)$$

These velocities $u_x, u_y, u_z, v_x, v_y, v_z, U_x, \&c.$, are measured with respect to some definite system of "space time" coordinates. An observer moving past this system of coordinates with the velocity ϕ in the X direction would find

for the corresponding component velocities the values

$$\frac{u_x - \phi}{1 - \frac{u_x \phi}{c^2}}, \quad \frac{\sqrt{1 - \phi^2/c^2} u_y}{1 - \frac{u_x \phi}{c^2}}, \quad \frac{\sqrt{1 - \phi^2/c^2} u_z}{1 - \frac{u_x \phi}{c^2}}, \quad \frac{v_x - \phi}{1 - \frac{v_x \phi}{c^2}}, \quad \&c.,$$

given by Einstein's transformation equations.

Since the laws of the conservation of mass and momentum must also hold for the measurements of this new observer, we may write the following new relations corresponding to equations 1 to 4:--

$$\begin{aligned} & m_0 f \left\{ \left(\frac{u_x - \phi}{1 - \frac{u_x \phi}{c^2}} \right)^2 + \left(\frac{\sqrt{1 - \phi^2/c^2} u_y}{1 - \frac{u_x \phi}{c^2}} \right)^2 + \left(\frac{\sqrt{1 - \phi^2/c^2} u_z}{1 - \frac{u_x \phi}{c^2}} \right)^2 \right\} \\ & + n_0 f \left\{ \left(\frac{v_x - \phi}{1 - \frac{v_x \phi}{c^2}} \right)^2 + \left(\frac{\sqrt{1 - \phi^2/c^2} v_y}{1 - \frac{v_x \phi}{c^2}} \right)^2 + \left(\frac{\sqrt{1 - \phi^2/c^2} v_z}{1 - \frac{v_x \phi}{c^2}} \right)^2 \right\} \\ & = m_0 f \left\{ \left(\frac{U_x - \phi}{1 - \frac{U_x \phi}{c^2}} \right)^2 + \left(\frac{\sqrt{1 - \phi^2/c^2} U_y}{1 - \frac{U_x \phi}{c^2}} \right)^2 + \left(\frac{\sqrt{1 - \phi^2/c^2} U_z}{1 - \frac{U_x \phi}{c^2}} \right)^2 \right\} \\ & + n_0 f \left\{ \left(\frac{V_x - \phi}{1 - \frac{V_x \phi}{c^2}} \right)^2 + \left(\frac{\sqrt{1 - \phi^2/c^2} V_y}{1 - \frac{V_x \phi}{c^2}} \right)^2 + \left(\frac{\sqrt{1 - \phi^2/c^2} V_z}{1 - \frac{V_x \phi}{c^2}} \right)^2 \right\}. \quad (1a) \end{aligned}$$

$$\begin{aligned} & m_0 f \left\{ u_x \dots \right\} \frac{u_x - \phi}{1 - \frac{u_x \phi}{c^2}} + n_0 f \left\{ v_x \dots \right\} \frac{v_x - \phi}{1 - \frac{v_x \phi}{c^2}} \\ & = m_0 f \left\{ U_x \dots \right\} \frac{U_x - \phi}{1 - \frac{U_x \phi}{c^2}} + n_0 f \left\{ V_x \dots \right\} \frac{V_x - \phi}{1 - \frac{V_x \phi}{c^2}}. \quad (2a) \end{aligned}$$

$$\begin{aligned} & m_0 f \left\{ u_x \dots \right\} \frac{\sqrt{1 - \phi^2/c^2} u_y}{1 - \frac{u_x \phi}{c^2}} + n_0 f \left\{ v_x \dots \right\} \frac{\sqrt{1 - \phi^2/c^2} v_y}{1 - \frac{v_x \phi}{c^2}} \\ & = m_0 f \left\{ U_x \dots \right\} \frac{\sqrt{1 - \phi^2/c^2} U_y}{1 - \frac{U_x \phi}{c^2}} + n_0 f \left\{ V_x \dots \right\} \frac{\sqrt{1 - \phi^2/c^2} V_y}{1 - \frac{V_x \phi}{c^2}}. \quad (3a) \end{aligned}$$

$$\begin{aligned} & m_0 f \left\{ u_x \dots \right\} \frac{\sqrt{1 - \phi^2/c^2} u_z}{1 - \frac{u_x \phi}{c^2}} + n_0 f \left\{ v_x \dots \right\} \frac{\sqrt{1 - \phi^2/c^2} v_z}{1 - \frac{v_x \phi}{c^2}} \\ & = m_0 f \left\{ U_x \dots \right\} \frac{\sqrt{1 - \phi^2/c^2} U_z}{1 - \frac{U_x \phi}{c^2}} + n_0 f \left\{ V_x \dots \right\} \frac{\sqrt{1 - \phi^2/c^2} V_z}{1 - \frac{V_x \phi}{c^2}}. \quad (4a) \end{aligned}$$

It is evident that these equations (1a-4a) must be true no matter what the velocity between the original system of coordinates and the new observer, that is they are true for all values of ϕ . The velocities $u_x, u_y, u_z, v_x, \&c.$, are, however, perfectly definite quantities, measured with reference to a definite set of axes and entirely independent of ϕ . If these equations are to be true for perfectly definite values of $u_x, u_y, u_z, v_x, \&c.$, and for all values of ϕ , it is evident that the function $f(\)$ must be of such a form that the equations are identities in ϕ . As a matter of fact ϕ can be cancelled from all the equations if we make $f(\)$ of the form

$$\frac{1}{\sqrt{1 - \frac{v^2}{c^2}}}; \text{ and we see that the expected relation is a}$$

solution of the equations. Although this does not exclude the possibility that there may be other solutions of these functional equations, nevertheless from a consideration of the complexity of the equations it appears doubtful if any other simple function would satisfy the necessary requirements.

In conclusion it is to be noted that in these derivations no reference has been made to any electrical charge which might be carried by the body whose mass is to be determined. Hence, if these considerations are correct, we may reject the possibility of explaining the Kaufmann-Bucherer experiment by assuming that the charge of a body decreases with its velocity*, since the increase in mass is alone sufficient to account for the results of the measurements.

Cincinnati, Ohio.

October 31, 1911.

XXXIV. *Theory of the Behaviour of the Quadrant Electrometer.* By Prof. A. ANDERSON †.

THE following presentation of the theory of the quadrant electrometer has, it seems to me, the merit of simplicity, and consequently may be of use to those who are engaged in working with the instrument. The theory given by Mr. G. W. Walker (Phil. Mag. Aug. 1903) is perhaps not elementary enough for the general reader, and the incidental reference to the subject by Prof. Sir J. J. Thomson in a paper on the Charge of Electricity carried by the Ions

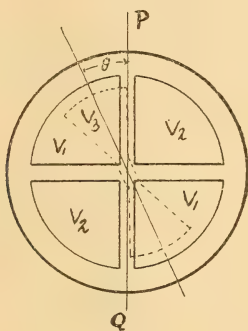
* The possibility of explaining the Kaufmann-Bucherer experiment by assuming that the electrons have less charge at higher velocity was suggested by Professor More of this University: Phil. Mag. xxi. p. 196 (1911).

† Communicated by the Author.

produced by Röntgen Rays (Phil. Mag. Dec. 1898) only deals with a particular problem which arose in the course of the experiments therein described.

Fig. 1 requires no explanation. It is merely a plan of the electrometer, the circle outside representing the metallic case. If V_1, V_2, V_3 denote the potentials of the two pairs of

Fig. 1.



quadrants and the needle, the corresponding charges are given by the equations

$$Q_1 = C_{11}V_1 + C_{12}V_2 + C_{13}V_3,$$

$$Q_2 = C_{12}V_1 + C_{22}V_2 + C_{23}V_3,$$

$$Q_3 = C_{13}V_1 + C_{23}V_2 + C_{33}V_3.$$

Suppose the case of the instrument to be earthed, that $V_2 > V_1$, and that the axis of figure of the needle makes an angle θ with QP in the position of equilibrium, and suppose also that θ vanishes when everything is earthed. A very little consideration will make it clear that, up to and including the second power of θ , we have

$$C_{11} = b + \beta\theta, \quad C_{12} = -(c + p\theta^2),$$

$$C_{13} = -(a + \alpha\theta), \quad C_{22} = b - \beta\theta,$$

$$C_{23} = -(a - \alpha\theta), \quad C_{33} = 2a + q - \kappa\theta^2.$$

C_{33} , it may be remarked, is the charge on the needle when $V_3 = 1$, and $V_2 = V_1 = 0$. The greater part of the complementary negative charge is on the quadrants and is equal to $-2a$; the rest, $-q + \kappa\theta^2$, is on the case of the instrument in the neighbourhood of P and Q. In the symmetrical position the charge on the needle will be $2a + q$, the charge on each pair of quadrants $-a$, and the charge on the case $-q$. If not in the symmetrical position, the charge on the case will

be less, and κ , which is an important factor in determining the sensibility of the electrometer, is numerically the decrease in this negative charge per unit increase of θ^2 . If F be the torsion couple required to turn the lower end of the suspension fibre through unit angle, we have

$$(F + \kappa V_3^2 + 2pV_1V_2)\theta = (V_2 - V_1)[2\alpha V_3 - \beta(V_1 + V_2)].$$

But, evidently, θ must vanish when $V_2 - V_3 = V_3 - V_1$, and therefore $\alpha = \beta$, and

$$(F + \kappa V_3^2 + 2pV_1V_2)\theta = 2\alpha(V_2 - V_1)\left(V_3 - \frac{V_1 + V_2}{2}\right).$$

If $V_2 = 0$, this equation becomes

$$\theta = \frac{2\alpha V_2\left(V_3 - \frac{V_2}{2}\right)}{F + \kappa V_3^2}.$$

If V_2 can be neglected in comparison with V_3 ,

$$\theta = \frac{2\alpha V_2 V_3}{F + \kappa V_3^2},$$

which, for a given value of V_2 is maximum when

$$F = \kappa V_3^2, \quad \text{or} \quad V_3 = \sqrt{\frac{F}{\kappa}},$$

the condition of maximum sensibility.

It will be interesting now to consider the case where, as often happens, the axis of figure of the needle is not strictly along QP when everything is earthed. Let the angle which it makes with QP be γ , and let γ be measured in the direction from the pair of quadrants whose potential afterwards becomes V_2 to the pair whose potential afterwards becomes V_1 . θ will now be measured, not from QP, but from the position of the axis of the needle when everything is earthed. The values of C_{11} , C_{12} , &c., will be obtained by writing $\theta + \gamma$ for θ and

$$(F + \kappa V_3^2 + 2pV_1V_2)\theta = 2\alpha(V_2 - V_1)\left[V_3 - \frac{V_1 + V_2}{2}\right] - 2\gamma(\kappa V_3^2 + 2pV_1V_2),$$

which, when $V_1 = 0$ and V_2 is very small in comparison with V_3 , reduces to

$$\theta = \frac{2\alpha V_2 V_3 - 2\gamma\kappa V_3^2}{F + \kappa V_3^2}.$$

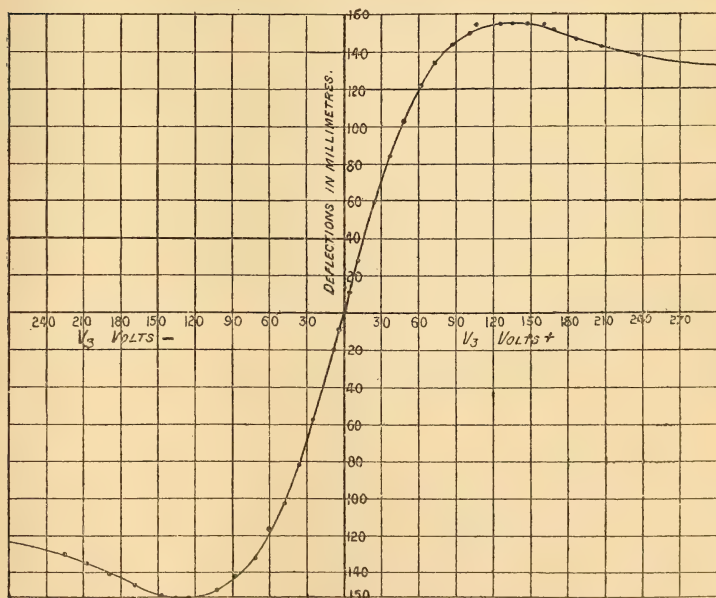
When both quadrants are earthed the value of θ is

$$\frac{-2\gamma\kappa V_3^2}{F + \kappa V_3^2},$$

which $= -\gamma$ when $F = \kappa V_3^2$. Thus, when the potential which makes the needle most sensitive is put on, while both quadrants remain earthed, the needle moves into the symmetrical position. If V_3 is less than this value it will move past the symmetrical position, and if greater, not so far. If the potentials of the quadrants be interchanged, V_1 becoming V_2 and V_2 zero, so that the deflexion is in the opposite direction, the value of θ is increased. The two deflexions will not be equal, the greater deflexion being when the needle, in its motion from rest, passes through the symmetrical position. The difference of these deflexions when the needle is most sensitive is equal to 2γ .

The curve shown in fig. 2 gives the deflexion in millimetres of the scale when a potential of about .25 volt was put on to one pair of quadrants, the other pair being earthed. The potential of the needle was varied from -270 volts to $+270$ volts.

Fig. 2.



The deflexion apparently due to γ was made as nearly as possible zero, but when it was made to vanish when V_3 was positive it was found not to vanish when V_3 was negative, and, in fact, it seemed to depend on the potential V_3 of the needle. For instance, when V_3 was $= -148$ volts and both pairs of quadrants earthed the deflexion was 2 millimetres to

the left, but when V_3 was $= +148$ volts it was 15 millimetres in the same direction. The instrument was surrounded by an earthed metallic box to screen it from external influences. In the experiment, the result of which is given in fig. 2, the deflexions, which are measured from the resting point in each case, were not exactly equal but always differed by a small quantity. When, for example, $V_3 = +100$ volts the deflexion was 150 mm. to the left, but when $V_3 = -100$ volts it was 148 mm. to the right. The first result is plainly inconsistent with the formula

$$\theta = \frac{2\alpha V_2 \left(V_3 - \frac{V_2}{2} \right) - 2\gamma\kappa V_3^2}{F + \kappa V_3^2},$$

which, when V_2 vanishes, should give the same value of θ whether V_3 is positive or negative, provided its numerical value is not altered.

As a matter of fact, there is another effect quite as important as the existence of γ which, I believe, is always present. It is certainly present in the Dolezalek electrometers in my possession, and in one of them it is very marked. This effect is due to the existence of a contact-difference of potential between the two pairs of quadrants. In other words, when the needle and both pairs of quadrants are earthed there is still a difference of potential between the air in contact with one pair of quadrants and the air in contact with the other pair. Suppose this difference to be r . Then, denoting by V_3 the potential of the air in contact with the needle, we have

$$\theta_0 = \frac{2\alpha r \left(V_3 - \frac{r}{2} \right) - 2\gamma\kappa V_3^2}{F + \kappa V_3^2},$$

for the deflexion when both quadrants are earthed. Here θ is measured from the position which the needle would occupy if both V_3 and r were zero. If V_3 be made negative without changing its numerical value, which it may be remarked cannot be done by connecting the needle with the negative pole of the battery instead of with the positive, as there is always a difference of potential between the needle and the air in contact with it, we get for the deflexion

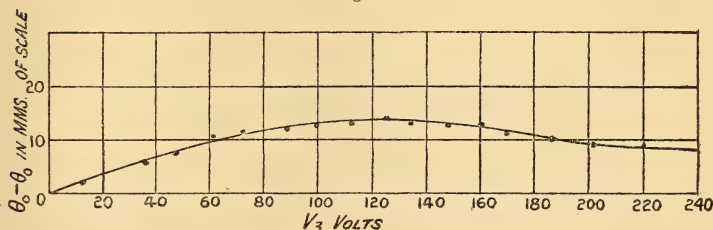
$$\theta_0' = \frac{2\alpha r \left(-V_3 - \frac{r}{2} \right) - 2\gamma\kappa V_3^2}{F + \kappa V_3^2}.$$

Hence

$$\theta_0 - \theta'_0 = \frac{4\alpha r V_3}{F + \kappa V_3^2},$$

which is independent of γ .

Fig. 3.



The curve in fig. 3 is plotted from the observed values of $\theta_0 - \theta'_0$ in the above experiment. It will be noted that $\theta_0 - \theta'_0$ is maximum when the potential of the needle is that which corresponds to maximum sensitiveness, which it ought to be, since, when both pairs of quadrants are earthed, we are merely obtaining the deflexion of the needle due to their contact-difference of potential.

The formula given above for θ is correct, if it be understood that V_1 , V_2 , and V_3 are the potentials of the air in contact with the quadrants and the needle, θ being measured from the position which the needle occupies when V_1 , V_2 , V_3 are all zero, and zero potential being the potential of the air in contact with the case of the instrument.

Comparing fig. 3 and fig. 2, it will be seen that the contact-difference of potential between the pairs of quadrants was about .01 volt. The contact-difference of potential between two specimens of the same metal might differ by much more than this.

XXXV. *The Micro-Azimometer; an Instrument for measuring small Angular Displacements.* By C. V. BURTON, D.Sc.*

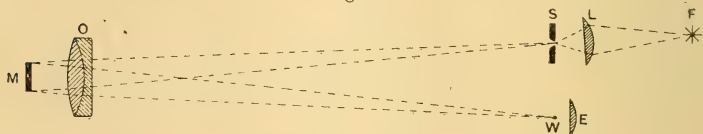
1. **T**HE chief object of the device here described is to increase the sensitiveness of reflecting instruments by optical means, especially when the available reflecting surface is but small. Thus it has been found possible, when the (rectangular) aperture of the mirror measures 3.5 mm. wide $\times$ 4 mm. high, to fix the azimuth of the mirror with a

* Communicated by the Author.

maximum error of 0.1 second of arc, and with a probable error, in a single setting, of 0.042 second. It should be said at once that the flatness of the mirror was in this case practically perfect, the reflecting surface being that of a silvered glass flat, with a stop placed before it; on the other hand, an acetylene flame was used as the source of illumination, and this is greatly inferior in intrinsic brightness to various incandescent filaments emitting white light. As will appear later, the intrinsic brightness of the source has an important influence on the attainable precision of reading.

2. It might at first sight appear that the results just referred to were not easily to be reconciled with known optical principles, according to which the most accurately focussed image is a system of diffraction patterns, and magnification carried beyond certain limits ceases to be of use, owing to the proportionate increase of diffuseness of the image. But it is by taking advantage of the peculiarities of diffraction patterns that increased refinement in fixing the azimuth of a mirror may be secured; and to this end it is found convenient to use high magnifications.

Fig. 1.



3. Fig. 1 is a diagrammatic plan view of the apparatus used. F is a small acetylene flame, an image of which is focussed by the lens L upon a narrow vertical slit S. This is at the principal focus of the object-glass O; light which has passed through S and O being reflected from a plane mirror M of rectangular outline, and refocussed in the neighbourhood of the vertical wire W. On looking through an eyepiece E*, a diffraction pattern is seen, consisting of vertical bands: a central white band, separated by very dark almost black intervals from the coloured bands which fade off on each side. Either the slit S†, or the frame

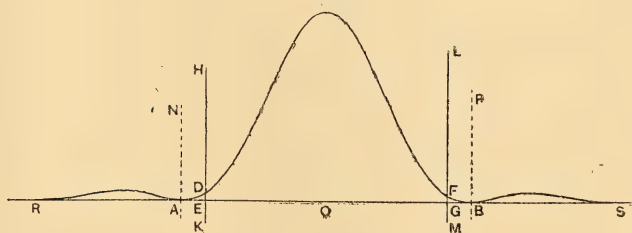
* As will appear below (§ 10), this is preferably a cylindrical lens with its generating lines vertical.

† Before the slit S a refracting prism (not shown) was fixed, so that the illuminating arrangements could be kept clear of the observer's head. The condensing lens L was carried upon a bracket which moved with the slit, while the flame F was burnt from a jet which could be independently moved along a slide parallel to WS until the best illumination of the field was secured.

carrying the wire W, is capable of micrometric adjustment along a straight slide, whose line of motion is WS. By these means the wire W may be brought with considerable precision to the middle of the diffraction pattern, and the reading of the micrometer noted. It is essential to sensitiveness that the width of the wire should be so chosen that, in correct adjustment, the central bright band is *almost completely obliterated*, only a faint "residual strip" of light appearing on each side between the wire and the adjacent dark of the pattern. When this condition is fulfilled, a displacement of the wire amounting to a very small fraction of the width of the central band will produce a perceptible inequality in the brightness of the "residual strips." If the wire employed is too thick, the sensitiveness will be *increased* by placing a stop before the mirror, so as to reduce the width of the reflecting surface, and thus spread out the diffraction pattern to suit the diameter of the wire.

4. *When the illumination is monochromatic, and the slit ideally narrow*, the distribution of brightness in the diffraction pattern is that indicated in fig. 2. Abscissæ, reckoned from O, represent distance measured horizontally in the focal plane from the median line of the pattern, and ordinates represent the corresponding brightness. AB is the

Fig. 2.



width of the central bright band, and is equal to $2\lambda f/a$, where λ is the wave-length of the light, f the focal-length of the object-glass, and a the width of the mirror. The curve of brightness touches the axis of abscissæ at A and B, corresponding to lines of absolute blackness in the pattern. Now suppose that a vertical wire HK, LM is placed so as to hide the central portion of the pattern, the axis of the wire being in the focal plane, and its diameter only slightly less than AB. Thus the areas ADE, FGB will represent the integral brightness (per unit of vertical length) of the

residual strips of light to be seen between the wire and the lines of blackness on either side of it.

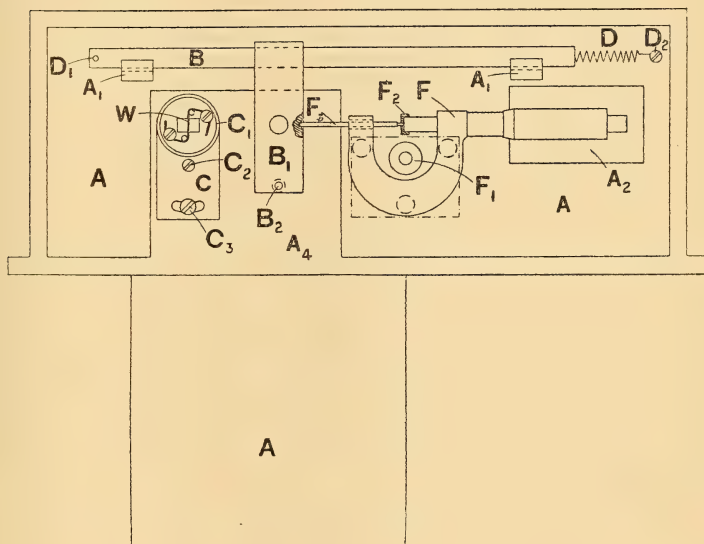
5. If the wire is displaced laterally, one of these residual strips will become brighter and the other fainter, and AE, GB being small compared with AB, it is evident that a displacement of the wire through a distance which is only a small fraction of AB may cause the ratio of integral brightness (area ADE : area FGB) to deviate considerably from unity. It appears indeed that, *when the illumination is homogeneous, the sensitiveness of the arrangement is limited only by the intrinsic brightness of the source* (cf. § 31).

6. Some particulars of the actual apparatus may here be given. The focal length of the achromatic objective O (fig. 1) was 55 cm. The mirror M was constituted by a silvered glass flat, between which and the objective was a screen pierced by a rectangular hole with bevelled edges. The hole itself measured 5.8 mm. wide $\times$ 4 mm. high ; but the screen was so supported that it could be turned about a vertical axis into an oblique position, thus reducing the width of the effective reflecting surface. In this way a suitable relation could be secured between the scale of the diffraction pattern in the focal plane WS and the thickness of the wire W. Since W and S were some 5 cm. apart, the distance of the perforated screen from the mirror, as well as the obliquity of the screen, must be taken into account in calculating the effective width of reflecting surface, which was found to be 3.5 mm. The wire used was of copper and 0.176 mm. in diameter. E was either an ordinary eyepiece of 16 mm. equivalent focal length, or preferably a cylindrical lens of crown glass of about 15 mm. equivalent focal length. Stray light was excluded : the only light reaching the eye through E was that which had originally passed through S, and the observations were made in a fairly dark cellar.

7. The details of construction at the eye end of the apparatus, though of rather a makeshift description, may be worth mention, as the performance was, mechanically speaking, quite satisfactory, and others may perhaps wish to put a micrometer together on similar lines. In fig. 3, A is a flat cast-iron plate, whose plane is vertical. F is a Brown and Sharpe micrometer calliper, which is secured between A and a clamping-plate (shown in chain-dot) by means of the stud and nut F₁. To avoid straining the frame of the calliper, a seat for it is formed by three little bosses cast upon the plate A, and the clamping-plate has three corresponding bosses upon its inner side. The

recess A_2 provides sufficient room for the fingers when the setting of the micrometer has to be altered. The "anvil" of the calliper has been removed, and through the hole thus left the link F_3 passes clear. The right-hand end of F_3

Fig. 3. Scale 1:3.5.



bears directly against the end of the measuring-spindle, and is centred by passing through the cap F_2 . The left-hand end of F_3 is hemispherical, and rests in a conical depression in the side of the flat plate B_1 , on which the slit (not shown) is mounted. B_1 is attached to a tube B , which has been turned truly cylindrical, and rests in V's planed in the two lugs A_1A_1 of the plate A . A screw B_2 is screwed into B_1 from behind, and the head of this screw is kept in contact with the planed face A_4 by the weight of B and of the slit which it carries. Thus the motion of the system BB_1 is geometrically limited to displacements to right and left.

8. A coiled wire spring D passes axially through the tube B , and has one end attached to the pin D_1 , its other end being secured to the fixed screw D_2 . The tension of this spring remains fairly uniform throughout the range of motion of the micrometer, and is sufficient to ensure that the link F_3 shall be always in compression. Thus F_3 and the slit carried by the plate B_1 partake of the axial motion of the micrometer spindle. The wire W is fixed just in front

of the plate C in the manner indicated; it passes partly around two fixed upstanding pins, and is clamped under the heads of two screws. C_1 is a draw-tube in which an eyepiece (not shown) can be inserted. To adjust the verticality of the wire W, the plate C_2 can be slightly turned in its own plane about the screw C_2 as required, after which C_2 , C_3 are screwed home. It will be understood that the plate A is pierced with holes where required for the transmission of light. In the apparatus as actually used, the plate A was clamped to a cast-iron bedplate, at the further end of which the object-glass O and mirror M (fig. 1) were supported.

9. The micrometer calliper F could be read by estimation to 0.0001 inch; but for the tests which had to be made, much closer readings were required. These were obtained by means of a radial arm (not shown in fig. 3) which could be clamped at will upon the rotatable barrel of the micrometer, and the outer end of which rested always against the point of an auxiliary micrometer screw, the arm being approximately horizontal and the auxiliary screw vertical. The range of this extra-fine motion was about eight whole turns of the auxiliary screw, the head of which was divided into 100 parts. It was found that 530 of these parts were equivalent to 0.001 inch traverse of the main micrometer F.

10. Increased sensitiveness may be secured by means of any device which will increase the brightness of the diffraction pattern as seen under given lateral magnification. This is always true for homogeneous light, and in the case of illumination by white light the limit where increase of brightness ceases to be helpful has not yet been reached. Accordingly great advantage has been found in using as eyepiece a plano-convex cylindrical lens of crown glass, with generating lines vertical. The (vertical) length of slit illuminated then affects the brightness of the pattern seen, but not its apparent height, which is simply the apparent height of the mirror as regarded from the same view-point without the interposition of an eyepiece. There is, of course, a limit to the increase of brightness which can be effected by merely lengthening the slit; the limit is attained when the pencil of rays reaching the eye from each point of the mirror extends over the whole *height* of the pupil; and when a short-focus cylindrical eyepiece is used, the eye being thus brought fairly close to the primary focal plane, the condition is realized by a slit whose length is equal to the diameter of the pupil. If we take this to be only 3 mm., there should be a 25-fold gain of brightness when an ordinary

eyepiece of 16 mm. equivalent focus is replaced by a cylindrical lens.

11. Incidentally it may be remarked that the exchange of one cylindrical eyepiece for another of different focal length changes the brightness at any given point of the diffraction pattern inversely as the change of width of the pattern, the total brightness remaining unchanged for the whole pattern, and likewise unchanged for any defined fractional parts thereof, such as the residual strips of light which adjoin the wire when the micrometer is suitably adjusted and set. Hence, when a cylindrical lens serves as eyepiece, it does not appear that any disadvantage on the score of dimness should arise from the use of a fairly high lateral magnification.

12. When the slit is illuminated by white light, it is, of course, essential that the object-glass in front of the mirror be achromatic, if close readings of azimuth are to be possible; but, even so, since each homogeneous component of the pattern is on a scale proportional to the wave-length, the conditions must be far removed from those represented in fig. 2. There are, of course, no lines of absolute blackness corresponding to the points A, B, but when the familiar pattern is regarded from this point of view, it is to me surprising that so passable an appearance of blackness is presented on either side of the central bright band. The consistency with which the wire can be set centrally upon the pattern is certainly far beyond what I expected to be attainable with white light. Moreover, the dimness of the "residual strips" of light observed was distinctly felt to be a difficulty, and so it may well be that appreciably better results could be obtained with a source of white light more brilliant than an acetylene flame. Mr. S. D. Chalmers has suggested to me that *colour* may play an important part in aiding the judgment of the eye, for necessarily the "residual strips" differ from one another in colour as well as in general brightness when the setting is not quite central. I can by no means say that the effect referred to is inoperative, but only that I am not *aware* of a difference in colour when the setting is only just perceptibly imperfect.

13. Referring to the light-distribution curve (fig. 2) one would be inclined to think that, in judging of the relative brightness of the strips represented by AED, FGB, the eye must be considerably distracted by the greater total illumination of the adjoining subordinate bands RA, BS; and hence it might be expected that a marked advantage would be gained by the use of shutters extending from NA towards

the left, and from PB towards the right. Such shutters would, of course, be fixed relatively to the wire HK, LM, and would thus partake of any lateral displacement imparted micrometrically to the wire; the observer's view of the diffraction pattern being accordingly restricted to two narrow slits NA, HK and LM, PB. I cannot say that such an arrangement carefully constructed would not be helpful; but from a trial made with a hastily improvised pair of shutters, it did not appear likely that the gain of sensitiveness would outweigh the disadvantage of thus obliterating the lateral portions of the pattern; for in this case one could not be sure at a glance that it was indeed the strips AE, GB, which were in view. Possibly a useful compromise might be found in the use of shutters formed of dark, but not wholly opaque, glass.

14. The following tables give an analysis of readings taken to test the consistency with which settings could be made. Before each setting, the fine-adjustment head was turned back † at random, leaving a wide discrepancy between the wire and the centre of the diffraction pattern. The adjustment in the forward † direction was then continued until the setting appeared to be central, and the micrometer reading taken. The discrepancies in the readings must be attributed to errors of setting, combined with such as may have arisen from imperfections of the micrometric motion.

TABLE I.

Eye-piece: a cylindrical lens of 15 mm. equivalent focal length.

Effective surface of mirror 3.5 mm. wide $\times$ 4 mm. high.

Focal length of object-glass 55 cm.

Source of light: an acetylene flame.

Analysis of 10 successive settings.

	Greatest deviation from mean.	Quadratic mean deviation from mean.	Probable error of a single setting.
In position of reflected image:—			
(a) In millimetres.....	·00053	·00033	·00023
(b) In fractional parts of the width* of the central bright band	1/354	1/584	1/865
In azimuth of mirror (seconds) ...	0.10	0.062	0.042

* Calculated for λ_D .

† The terms "back" and "forward" are used conventionally.

TABLE II.

Ordinary eyepiece of 16 mm. equivalent focal length.
Effective surface of mirror 4 mm. $\times$ 4 mm.
Object-glass and illumination as in Table I.

Analysis of 7 successive settings.

	Greatest deviation from mean.	Quadratic mean deviation from mean.	Probable error of a single setting.
In position of reflected image :—			
(a) In millimetres.....	·00135	·00091	·00062
(b) In fractional parts of the width * of the central bright band }	1/122	1/180	1/266
In azimuth of mirror (seconds) ...	0·25	0·17	0·114

* Calculated for λ_D .

15. Trials with homogeneous light have not yet been made, as no sufficiently brilliant source has been available. Coloured glasses were tried, but the general loss of brightness far outweighed the advantage of approximate monochromatism.

16. A plane surface, reflecting light of wave-length λ , is generally considered sensibly true when its greatest deviation from planeness is within $\lambda/8$, corresponding to an extreme discrepancy of $\lambda/4$ in retardation. Once this degree of correctness has been attained, resolving-power, or sharpness of definition at a given focal length, cannot be substantially increased by a further approach to absolute flatness. But when we are attempting to discriminate azimuths with a fineness some hundreds of times as great as that which corresponds to the resolving-power, the demands upon the optical quality of the mirror and object-glass are necessarily far heavier. It is the mirror which presents difficulty; its necessary lightness in most suspensions rendering it difficult to ensure accurate figuring. Some suggestions on this and related points are contained in §§22, 23 below; meanwhile, it may be mentioned that a home-made mirror of iridio-platinum could have its azimuth fixed with an error which in no case exceeded 0·5 second, the mirror being 3·9 mm. wide $\times$ 3·1 mm. high, with a thickness of 0·23 mm. In this case the source of light was the flame of a paraffin lamp.

17. A micrometric device, such as that described, would necessarily be inapplicable in certain uses of reflecting instruments, even though a large gain of sensitiveness might be desirable. For example, the throws of a reflecting ballistic galvanometer could not be so read, unless we were content to set the micrometer laboriously by trial and error, so that, on depressing a key (or what not), the extreme excursion of the mirror just brought about bisection of the diffraction pattern by the wire.

18. It would, however, be practicable to deal with changes of azimuth which took place slowly enough to be adequately recorded by readings taken every few minutes. In such a case the micrometer could from time to time be set in advance, and the instant noted when bisection of the diffraction pattern was observed.

19. But micrometric methods find a more obvious application where the deflexions to be observed are steady, or so slowly changing as to allow of a setting being readily made at any given time. In many cases the instrument to be read (say, a radio-micrometer, or a galvanometer connected to a linear thermopile) would be furnished with a relatively stiff suspension, so that the greatest deflexion to be observed would come within the range of the micrometric traverse. If this were 25 mm., there should be no difficulty in reading deflexions correct to $1/25000$ part of the maximum deflexion observable *; a single micrometer screw of 0.5 mm. pitch, with head divided into 50 parts, should suffice. Incidentally there might be the advantage of a reduced instrumental period.

20. Above all, reflecting instruments used as detectors appear to be a promising field for the micro-azimometer, as I have ventured to call it. In place of a micrometer, an uncalibrated fine-motion screw here suffices to reset the zero from time to time if required. In relative resistance measurements it may be said that the limits of attainable accuracy are imposed directly and indirectly by the galvanometer. If we have the means of making the current in the bridge many times less, while the sensitiveness to lack of balance is at the same time greatly increased, a marked improvement in accuracy may be expected. This is especially the case in bolometer and resistance-thermometer work, where the temperatures of certain resistance-wires are the quantities which directly concern us.

* Always assuming an accurately made (or calibrated) micrometer, and a sensibly flat mirror of rectangular outline.

21. It is generally recognized as desirable that the mirror of a reflecting instrument should be as light as possible, and should have a small moment of inertia; but I venture to think that, in many cases where the most favourable relation between sensitivity and period is desired, it will be found advisable to tolerate the somewhat increased thickness of mirror which may be essential to accurate planeness. The vertical dimension of the reflecting surface referred to in Table I. could probably have been reduced from 4 to 2 or 3 mm. without impairing the closeness of the settings; but even where the very lightest suspensions have to be used, these micrometric methods can be made available by a slight modification.

22. This consists in the introduction of a short-focus *objective cylindrical lens*, with generating lines horizontal, between the object-glass O (fig. 1) and the mirror M; the latter being at the principal focus of the cylindrical lens. Thus the light emerging from a slit r mm. high would be condensed into a horizontal band in the plane of the mirror, the (vertical) breadth of this band being rg/f , where g is the focal length of the objective cylindrical lens. Accordingly the vertical dimension of the mirror might easily be reduced to (say) 0.5 mm., and yet an eye placed not far behind the wire W (fig. 1) would see the whole height of the objective cylindrical lens filled with light; the horizontal extent of the light-patch being, of course, limited to the breadth of the mirror. For the height of the objective cylindrical lens, 4 or 5 mm. should in all ordinary cases be ample; for convenience its breadth should be rather greater than that of the mirror. The appearance is then the same as if the height of the mirror were some 4 or 5 mm., and this also remains true when the field is viewed through a cylindrical or other eyepiece.

23. As regards the aberrations thus introduced, those which concern the vertical components of rays are of no consequence, so long as full illumination is secured over a sufficient vertical height of the diffraction pattern. Even the mirror need not be truly plane, provided all horizontal sections of its reflecting surface are parallel straight lines. To avoid aberrations which might be detrimental, the wire W and slit S (fig. 1) should be in the same vertical line, and the objective cylindrical lens should be set with its generating lines horizontal and at right angles to the beam transmitted by the object-glass O. It is quite easy to arrange that the last-named condition shall still be automatically satisfied when a change in the azimuth of the mirror makes it necessary

to adjust the position of the carriage on which both W and S are mounted.

24. Finally, it may be pointed out that, although the slit is illuminated as intensely as possible, its length need not be more than 3 or 4 mm., while its width has to be made exceedingly small; so that the heating and other disturbances due to radiation falling on the mirror are reduced to a minimum. This may become a matter of some importance when sensitivities are being pushed to extremes. In regard to the mirror, it may be well once again to emphasise the importance of a good optical surface of uniform reflecting power, and to repeat that the boundary of that surface must be a rectangle whose sides are respectively vertical and horizontal. Notwithstanding the name suggested for the apparatus described, its applicability is clearly not limited to the detection and measurement of azimuthal deflexions.

APPENDIX.

Approximate Theory of the Instrument.

25. In the case where the slit is illuminated by homogeneous light, it is not difficult to develop an approximate theory of the instrument; from this some qualitative conclusions may be drawn as to the performance to be expected when white light is substituted. The slit, on which the image of a luminous body is focussed, may be regarded as made up of innumerable independent point-sources. Corresponding to any one such point-source, a diffraction pattern is formed about the position of the "geometrical" image, the brightness B of which at any point, in terms of the central brightness B_0 , is given by

$$B = B_0 \frac{\lambda^2 f^2}{\pi^2 a^2 x^2} \sin^2 \frac{\pi a x}{\lambda f} \cdot \frac{\lambda^2 f^2}{\pi^2 h^2 y^2} \sin^2 \frac{\pi h y}{\lambda f} \quad \dots \quad (1)$$

Here x and y are respectively horizontal and vertical co-ordinates in the focal plane, the origin being the point representing the geometrical image; λ is the wave-length of the light employed, and f the focal length of the lens, while a is the breadth and h the height of the effective reflecting surface. The pattern thus represented is traversed by lines of absolute blackness, parallel to the axes of coordinates.

26. If, instead of a single point source of light, we have an infinitely narrow uniformly illuminated slit, whose length (l) is vertical and is considerable in comparison with $\lambda f/a$,

the illumination throughout a height l of the diffraction pattern becomes sensibly independent of y , and in place of (1) we have for the brightness

$$\text{where} \quad \left. \begin{aligned} B &= B_0 \sin^2 \theta / \theta^2 \\ \theta &\equiv \pi a x / \lambda f \end{aligned} \right\} \dots \dots \dots (2)$$

27. Since in practice the width of the slit must be finite, let X be a coordinate measured horizontally in the plane of the slit, and let

$$\phi \equiv \pi a X / \lambda f; \dots \dots \dots (3)$$

the width of the slit extending from $\phi = -\beta$ to $\phi = \beta$. Corresponding to any elementary width $d\phi$ of the slit, the brightness at any position θ in the focal plane is

$$C \frac{\sin^2 (\theta - \phi)}{(\theta - \phi)^2} d\phi; \dots \dots \dots (4)$$

where C is a constant which contains as a factor the brightness of illumination of the slit*. At any point whose coordinate is θ , the resultant brightness is found by integrating (4) from $\phi = -\beta$ to $\phi = \beta$; and as we shall only be concerned with values of θ fairly close to $\pm\pi$, while for a slit suitably narrowed for observation ϕ is small, no very great error will be introduced by taking the denominator $(\theta - \phi)^2$ as constant throughout the integration and equal to π^2 . Putting, for example,

$$\theta = -\pi + \gamma \text{ where } \gamma \text{ is small,}$$

the integral has the approximate value

$$\frac{C}{\pi^2} (2\gamma^2\beta + \frac{2}{3}\beta^3),$$

which, to our degree of approximation, is a minimum when $\gamma = 0$; *i. e.*, when $\theta = -\pi$.

* Here, and in what follows, it is supposed that light is focussed on the slit under a sufficiently wide angle to ensure the full theoretical brightness, notwithstanding the spreading of the transmitted pencil by diffraction. In practice it would not be convenient to narrow the slit beyond a certain limit; when a very bright source was available, advantage would rather be gained by increasing the focal length f : a cylindrical lens being used as eyepiece. It must, however, be remarked that, in these circumstances, the apparent vertical height of the pattern is inversely proportional to f (*cf.* § 22).

28. In like manner, if T is the total brightness per unit of vertical length in a strip whose breadth extends from $\theta = -\pi$ to $\theta = -\pi + \alpha$, that is, from $\gamma = 0$ to $\gamma = \alpha$, we find approximately

$$T = \frac{2}{3} \frac{C}{\pi^2} (\beta \alpha^3 + \beta^3 \alpha). \quad (5)$$

If α changes in value from α to $\alpha + \delta\alpha$, the corresponding change in T is

$$\delta T = \frac{2}{3} \frac{C}{\pi^2} (3\beta \alpha^2 + \beta^3) \delta\alpha. \quad (6)$$

Suppose, then, that two narrow strips of illumination, such as here concern us, can be unmistakably seen to differ in strength when their total brightnesses are in the ratio $1 \pm n^{-1} : 1 \mp n^{-1}$, or in other words, when the wire HK, LM (fig. 2) is so far laterally displaced that $\delta T/T = 1/n$ at one side of it, with a corresponding contrary change at the other side. Then for critical discrimination we have

$$\frac{1}{n} = \frac{(3\beta \alpha^2 + \beta^3) \delta\alpha}{\alpha \beta (\alpha^2 + \beta^2)},$$

or

$$\delta\alpha = \frac{\alpha}{n} \frac{1 + \beta^2/\alpha^2}{3 + \beta^2/\alpha^2}.$$

29. Since the central bright band of the diffraction pattern extends from $\theta = -\pi$ to $\theta = \pi$, the maximum error in setting the wire centrally upon the pattern, expressed as a fraction of the width of the band, is

$$\frac{\delta\alpha}{2\pi} = \frac{\alpha}{2n\pi} \frac{1 + \beta^2/\alpha^2}{3 + \beta^2/\alpha^2}. \quad (7)$$

30. To make this expression a minimum, α and β must be adjusted by trial until the consistency of setting appears to be as great as possible; there is, however, a theoretical optimum relation between α and β which, on a certain assumption, is readily deduced. The assumption is that the visibility of a faint elongated object of very small apparent breadth depends on the product breadth $\times$ average brightness, that is, in our case, on the total luminosity per unit of vertical length, represented by T of equation (5). We suppose, in fact, that, for any one observer working under given conditions, the number n defined in § 28 is a function

of T only ; and it appears that, whatever value be assigned to T, the most favourable relation between α and β is given by

$$\beta^2/\alpha^2=1+\sqrt{3}.$$

When this relation is duly satisfied (7) reduces to

$$\frac{\delta\alpha}{2\pi} = \frac{\alpha}{2n\pi} \cdot \frac{2+\sqrt{3}}{4+\sqrt{3}} = \frac{\alpha}{2n\pi} \times 0.65. \quad . \quad . \quad (7a)$$

31. As an example, suppose that $\alpha/2\pi=1/40$ (the diameter of the wire being thus $19/20$ of the width of the central bright band), and that $n=20$, which implies that a 10 per cent. difference of brightness between the right-hand and left-hand "residual strips" could not escape detection. In this case $\delta\alpha/2\pi=1/1230$; or, in words, the greatest error which the eye could tolerate in the setting of the wire would amount to only $1/1230$ of the width of the central band. The conjectures on which this estimate is based appear hardly extravagant, if we suppose the most brilliant obtainable source of homogeneous light to be used ; and there seems to be at least a reasonable prospect that the results given in Table I. could thus be surpassed (indeed these probably do not represent the limit of sensitiveness attainable with intense white light). On the simple diffraction theory which has served for the calculations in this paper, the ultimate sensitiveness realizable with a given mirror, and with a light-source of given wave-length, should increase indefinitely with the intrinsic brightness, to the fourth root of which it should be proportional.

32. Given the intrinsic brightness of the source of illumination and the dimensions of the (rectangular) reflecting surface, it is easily shown that, within limits, the greatest attainable angular sensitiveness is independent of the focal length of the object-glass employed. For if, following a change in f , we make a proportional change in the width of the slit and the diameter of the wire, and an inversely proportional change in the equivalent focal length of the cylindrical eyepiece, the diffraction pattern, partially eclipsed by the wire, will be seen on the same lateral scale as before, and with the same brightness at every point. The only change observable in the field will be a reduction of the apparent *height* of the pattern as the focal length f is increased. It is only when the apparent height has been thus reduced below a certain limit that the sensitiveness will

become impaired. In that case it can, if desired, be restored by the use of an objective cylindrical lens (§ 22).

The method of detecting and measuring small angular displacements, which forms the subject of this paper, was developed in connexion with a "search for a new property of matter in motion," for which a grant was obtained through the Royal Society. I have also to thank the Earl of Berkeley for most kindly placing the resources of his laboratory workshop at my disposal.

Boars Hill, Oxford.

Nov. 1911.

XXXVI. *Ionization by Collision.*

By NORMAN CAMPBELL, *Sc.D.**

1. **T**HE theory of ionization by collision of ions and the application of it to explain the electrical discharge through gases at low pressures is due mainly to Townsend†. In the course of some recent work, described in the following paper, doubts have been thrown upon the accuracy of the mathematical argument by which his formulæ are derived from his physical assumptions. Those assumptions are not doubted, but since some of them are of sufficient interest to merit special consideration, Townsend's entire argument will be sketched briefly.

2. Townsend makes the following hypotheses:—

(1) An ion, positive or negative, formed by any means in a gas, will produce a fresh pair of ions when it collides with a neutral molecule, if previously to that collision it has fallen freely under the action of the electric field through a potential not less than some finite value V' . V' is much greater for positive than for negative ions. In what follows negative ions only will be under consideration, for it will be assumed that the electric fields are so small that there is no appreciable ionization by collision of the positive ions.

(2) An ion, after collision with a neutral molecule, whether or not that collision results in the production of fresh ions, retains no portion of its previous velocity, but starts again from rest; it retains, however, its charge. (The velocity of thermal agitation is so small compared with that acquired under the action of the field in all the cases considered that it may be neglected.)

* Communicated by the Author.

† Townsend's work in this direction is summarized in his volume 'The Theory of the Ionization of Gases by Collision' (Constable, London, 1910. References will be made throughout to this book).

(3) An ion, however formed, immediately after its formation has a velocity so small that it may be neglected.

(4) A collision, whether or not it results in ionization, does not change the nature of the ion in such a way that it is incapable of ionization at subsequent collisions after a free fall through the potential difference V' .

3. Assumption (1) is the basis of the theory. (2) is almost certainly not accurately true; an ion after collision retains some portion of its previous velocity; but the assumption is made for simplicity of calculation. The error probably does not lead to an error in the form of the formulæ deduced, but only to values of N or V' which are somewhat too small. (3) is considered at length in the following paper * on "Ionization by α rays."

(4) is deserving of further consideration. When the theory of gaseous ionization was first advanced by Thomson and Rutherford, it was believed that the negative ion consisted of a group of several molecules collected round an electron. Ionization was thought to consist in the liberation of an electron from a neutral molecule, the collection of other neutral molecules round it being effected at subsequent collisions. If this view, already considerably discredited, were correct, a negative ion immediately after its formation would be a system different from a negative ion which had already made several collisions. After these collisions it would resemble the positive ion more than the original electron. Accordingly, if the great difference in V' for the negative and positive ions is to be attributed to a difference in their structure, it would be expected that this difference should disappear after a few collisions, and that no ionization by collision of negative ions which had made such previous collisions would occur.

This view is not adopted by Townsend; he assumes that the properties of the negative ion remain unchanged however many collisions it makes. If his assumption is true, the conclusion would seem to follow that the negative ion must remain an electron throughout its history, and not collect round it neutral molecules. The theory will be developed first on this assumption; later it will be considered how the theory is modified if the negative ion changes its properties after a few collisions.

4. The gas is supposed to be contained between parallel electrodes, of which the distance apart, parallel to the axis of x , is l . The difference of potential between the electrodes is V , and the uniform electric intensity between them

* To be published in the April number.

$X = V/l$. Let $N = N_0 p$ be the number of collisions made by an ion in travelling 1 cm. in the direction of x ; p is the pressure of the gas. Then, if q_0 is the number of ions starting from the origin and q the number arriving without previous collision at x , we have, since $N dx$ is the number of collisions made in a layer dx ,

$$-\frac{dq}{dx} = qN, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\text{or} \quad q = q_0 e^{-Nx}. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Let b be the smallest distance through which the ions must fall freely in order to be able to ionize at the next collision, so that

$$b = \frac{V'l}{V} = \frac{V'}{X}. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Then e^{-Nb} is the chance that an ion starting from a given layer will travel a distance b parallel to x without making a collision, and $N e^{-Nb} dx$ is the chance that, after travelling freely for that distance, it will make a collision in a layer of thickness dx . Following Townsend, we shall write

$$\alpha = \alpha_0 p = N e^{-Nb}. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

5. Townsend now proceeds to argue as follows:—Let n_1 be the number of negative ions liberated per second at the surface of the positive electrode, $n_0 p dx$ the number liberated per second by the external ionizing agent (rays of various descriptions) in any layer of the gas of thickness dx at a pressure p . Let $f(x)$ be the number of ions entering from the positive side a layer of thickness dx at a distance x from the positive electrode per second. Then $f'(x) dx$ is the number of ions liberated per second in that layer. These ions are due to two agencies: first, the external ionizing agent, giving a number $n_0 p dx$; second, the collisions of ions liberated in previous layers which have travelled a distance not less than b before arriving at the layer. The number of these collisions Townsend makes equal to the number of ions passing through the layer per second multiplied by the chance that an ion travels a distance not less than b and then makes a collision. He thus obtains

$$f'(x) = n_0 p + \alpha f(x). \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Or, since $f(x) = n_1$, when $x = 0$,

$$f(x) = \left(n_1 + \frac{n_0}{\alpha_0} \right) e^{\alpha x} - \frac{n_0}{\alpha_0}. \quad . \quad . \quad . \quad . \quad (6)$$

The number arriving at the negative electrode is $f(l)$; so that, if i is the current received by that electrode and e the charge on an ion,

$$i/e = \left(n_1 + \frac{n_0}{\alpha_0} \right) e^{\alpha_0 l} - \frac{n_0}{\alpha_0}. \quad . \quad . \quad . \quad (7)$$

6. It is immediately clear that this formula cannot be completely accurate; for, if V is less than V' , there can be no ionization by collision according to the theory, and consequently $f(l)$ for all values of V less than V' should be constant and equal to $n_1 + n_0 p l$; this condition is not fulfilled by (7). A little consideration discloses the source of the error. Townsend assumes that the proportion of the ions passing through any given layer which have travelled freely a distance sufficient to enable them to ionize at their next collision is constant and independent of the position of the layer. This assumption cannot be true, for, if the layer is distant less than b from the positive electrode, none of the ions in that layer can possibly have travelled a distance b ; the frac ion is here zero, while elsewhere it is finite.

In order to estimate rightly the number of ions passing per second through the layer x which, having travelled freely a distance not less than b , will make collisions and produce fresh ions in that layer, we must consider, not the total number of ions passing through the layer x , but the total number passing through the layer $(x-b)$. As will be seen from § 4, αdx is not the chance that an ion in the layer x has travelled a distance b freely and makes a collision in that layer, but the chance that an ion in the layer x will travel a distance b freely and make a collision in the layer $(x+b)$; these two chances are not identical. The ions passing through any given layer are not a random collection in respect of the distance that they have travelled previously to arriving at that layer; for some of them are known to have been produced in the layer; but the ions in any given layer are a random collection in respect of the distance that they will travel after leaving the layer, for this distance is independent of the distance that they have travelled previously.

7. Accordingly, the number of ions passing per second through the layer x which produce fresh ions by collisions in it is the number passing through the layer $(x-b)$ per second multiplied by the chance that an ion in that layer travels a distance b and then makes a collision. In place of (5) we get

$$f'(x) = n_0 p + \alpha f(x-b). \quad . \quad . \quad . \quad (8)$$

8. This equation is an accurate expression of the theory, but, in order to solve it, it is necessary to depart from the theory. For if n_1 is finite, neither $f(x)$ or $f'(x)$ is continuous; both functions obviously have a discontinuity at $x=0$, and the form of (8) shows that they will also have a discontinuity at $x=mb$, where m is any integer. If $n_1=0$, but n' is finite, $f'(x)$, but not $f(x)$, will be discontinuous at $x=0$, but both functions will again be discontinuous at all values of m other than 0. Now it is possible to calculate accurately according to the theory what should be the current between electrodes a distance l apart in a gas at pressure p , when X has a given value, but the calculations are extremely complex, and the resulting formula for the relation between i, l, p, X is not of a form to which Townsend's measurements can be applied. We will therefore assume that $f(x)$ and $f'(x)$ are continuous, and examine the results we obtain.

If $f(x)$ is continuous it must have, in order to satisfy (8), the form

$$f(x) = A e^{\beta x} - \frac{n_0}{\alpha_0}, \quad \dots \quad (9)$$

$$\text{where} \quad \beta = \alpha e^{-\beta b}. \quad \dots \quad (10)$$

To determine A use must be made of a known value of $f(x)$ for some value of x . Now between $x=0$ and $x=b$, $f(x)$ must have the form

$$f(x) = n_1 + n_0 p x. \quad \dots \quad (11)$$

It is clear that no value of A will give this form to $f(x)$ for all values of x within the range, and a choice must be made. If we choose $x=0$ we get

$$A = n_1 + \frac{n_0}{\alpha_0}, \quad \dots \quad (12)$$

if we choose $x=b$ we get

$$A = \left\{ n_1 + n_0 \left(p b + \frac{1}{\alpha_0} \right) \right\} e^{-\beta b}. \quad \dots \quad (12')$$

Now, since we are concerned experimentally with the value of $f(x)$ for $x=l$, where l is greater than b , we are likely to get the more accurate results if we fit the curve to the larger value of x . Accordingly, taking (12') we get

$$i/l \epsilon = f(l) = e^{\beta l} \left\{ n_1 + n_0 \left(p b + \frac{1}{\alpha_0} \right) \right\} e^{-\beta b} - \frac{n_0}{\alpha_0}. \quad \dots \quad (13)$$

It is advisable to transform (13) slightly in order to apply it

to Townsend's measurements, where the values of X/p and not of X are given. Writing $X/p = z$, $\beta = \beta_0 p$ we have

$$pb = \frac{V'}{z} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (14)$$

$$\beta_0 = \alpha_0 e^{-\beta_0 \frac{V'}{z}} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (15)$$

$$\alpha_0 = N_0 e^{-N_0 \frac{V'}{z}} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (16)$$

$$i/\epsilon = e^{\beta_0 p l} \left\{ n_1 + n_0 \left(\frac{V'}{z} + \frac{1}{\alpha_0} \right) \right\} e^{-\beta_0 \frac{V'}{z}} - \frac{n_0}{\alpha_0} \cdot \cdot \cdot \quad (13')$$

It was noted that Townsend's formulæ were unsatisfactory because they did not lead to the right value of $f(l)$ when $V = V'$. The formula (13') obviously leads to the right value, for it has been fitted to $x = b$, and when $V = V'$ $l = b$. It also leads to the right value, $f(l) = n_1$ for all values of V when $p = 0$.

9. The only experiments by Townsend which are sufficiently detailed and accurate to enable a comparison to be made between equations (5) and (13') are those on ionization by ultra-violet light. In these conditions $n_0 = 0$, and both equations reduce to the simple exponential form

$$i/\epsilon = P e^{Ql}, \quad \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (17)$$

where, according to (5), $P = n_1$, $Q = \alpha$, and according to (13') $P = n_1 e^{-\beta b}$, $Q = \beta$.

n_1 is the value of i/ϵ when either $p = 0$ or V is less than V' ; but, since Townsend does not give the values of this quantity in his experiments, it is impossible to use it to test the two formulæ by a comparison of the observed and calculated values of P . The test must be made by means of Q . Townsend deduces from his equations the value of Q/p for a number of values of z , and then uses (4) to calculate values for N_0 and V' ; the concordance between the observed values of Q/p and the values of α_0 deduced from N_0 and V' is taken as a test of the accuracy of the theory. The same procedure can be adopted if $Q = \beta$; for we have the following equation to determine N_0 and V' from the relation between Q/p and z :—

$$\log \beta_0 + \beta_0 \frac{V'}{z} = \log N_0 - N_0 \frac{V'}{z} \cdot \cdot \cdot \cdot \cdot \quad (18)$$

This calculation has been carried out and the results are given in Tables I.—VIII. Townsend found that the calculated and observed values did not agree for small values

of z , and used only the larger values to determine N_0 and V' . The discrepancy is not nearly so marked if Q is taken as equal to β and not to α , but the same procedure has been adopted; only values of Q/p to the left of the asterisk have been used in computing the values of N_0 and V' .

At the head of each table are given the values of N_0 and V' deduced respectively on the assumption that $Q=\alpha$ and that $Q=\beta$. The first row of the table gives the value of z ; the second those of Q/p , the exponential coefficient given by the observations; the third and fourth rows give the differences between this observed value and the values of α_0 and β_0 respectively calculated from the appropriate values of N_0 and V' .

It may be noted that the comparison effected in the last two rows is rather more favourable to equation (5) than to (13'), for the greater complexity of the latter has made it necessary to adjust to a minimum the sum of the squares of the residuals of (18), and not $\Sigma(Q/p-\beta_0)^2$, whereas Townsend's figures are adjusted so that $\Sigma(Q/p-\alpha_0)^2$ is a minimum.

TABLE I.

Air.

$$(Q=\alpha) \quad N_0=14.6, \quad V'=25.0.$$

$$(Q=\beta) \quad N_0=17.93, \quad V'=19.00.$$

	1000	800	700	600	500	400	300	*	200	100
z	10.5	9.3	8.7	7.9	7.0	5.82	4.4		2.6	0.72
Q/p	10.5	9.3	8.7	7.9	7.0	5.82	4.4		2.6	0.72
$Q/p-\alpha$ calc. ...	+0.4	0.0	+0.1	0.0	0.0	0.03	+0.1		+0.26	+0.34
$Q-\beta$ calc.	+0.04	-0.08	+0.01	-0.01	-0.07	+0.02	+0.03		+0.04	+0.18

TABLE II.

Nitrogen.

$$(Q=\alpha) \quad N_0=12.4, \quad V'=27.6.$$

$$(Q=\beta) \quad N_0=16.70, \quad V'=21.30.$$

	600	500	400	300	200	100	*
z	600	500	400	300	200	100	
Q/p	7.0	6.2	5.2	3.95	2.3	.42	
$Q/p-\alpha$ calc. ...	0.0	-0.25	-0.1	0.0	+0.06	+0.01	
$Q/p-\beta$ calc. ...	-0.16	-0.08	0.0	+0.07	+0.06	-0.15	

TABLE III.

Hydrogen.

$$(Q=\alpha) \quad N_0=5.0, \quad V'=26.0.$$

$$(Q=\beta) \quad N_0=6.46, \quad V'=20.4.$$

z	400	300	200	100	50	*	30
Q/p	3.7	3.3	2.62	1.36	.36		.68
$Q/p-\alpha$ calc. ...	+0.06	+0.06	0.00	+0.01	-.01		+0.014
$Q/p-\beta$ calc.	-0.16	-0.04	+0.05	+0.05	-.04		+0.003

TABLE IV.

Carbon Dioxide.

$$(Q=\alpha) \quad N_0=20, \quad V'=23.3.$$

$$(Q=\beta) \quad N_0=22.7, \quad V'=17.0.$$

z	1200	1000	800	700	600	500	400	*	300	200	100
Q/p	13.7	12.6	11.0	10.2	9.1	7.8	6.4		4.8	2.8	0.82
$Q/p-\alpha$ calc. ...	+0.1	+0.1	-0.2	-0.1	-0.1	-0.1	+0.2		+0.56	+0.8	+0.62
$Q/p-\beta$ calc.	-0.16	-0.14	+0.09	+0.01	+0.08	-0.2	+0.1		+0.01	+0.17	+0.20

TABLE V.

Hydrochloric Acid.

$$(Q=\alpha) \quad N_0=22.2, \quad V'=16.5.$$

$$(Q=\beta) \quad N_0=25.03, \quad V'=12.14.$$

z	1500	1000	800	700	600	500	400	*	300	200	100
Q/p	17.5	15.4	14.0	13.0	11.9	10.5	8.9		6.8	4.1	1.21
$Q/p-\alpha$ calc. ...	0.0	0.0	0.0	-0.2	-0.1	-0.15	-0.0		+0.3	+0.6	+0.64
$Q/p-\beta$ calc. ...	-0.12	+0.05	+0.15	+0.04	+0.04	-0.05	-0.02		-0.07	-0.0	

TABLE VI.

Water Vapour.

$$(Q=\alpha) \quad N_0=12.9, \quad V'=22.4.$$

$$(Q=\beta) \quad N_0=14.12, \quad V'=15.80.$$

z	1000	900	800	700	600	500	400	*	300	200	100
Q/p	9.7	9.4	9.0	8.5	7.95	7.2	6.35		5.2	3.6	1.31
$Q/p-\alpha$ calc. ...	0.0	+0.05	+0.1	-0.04	-0.01	0.0	+0.10		+0.3	+0.6	+0.60
$Q/p-\beta$ calc. ...	+0.01	+0.06	+0.05	+0.03	-0.04	0.00	+0.04		+0.08	+0.09	+0.06

TABLE VII.

Argon.

$$(Q=\alpha) \quad N_0=13.6, \quad V'=17.3.$$

$$(Q=\beta) \quad N_0=15.54, \quad V'=12.62.$$

z	600	500	400	300	200	[*] 100	50
Q/p	9.2	8.5	7.5	6.2	4.4	2.0	0.58
$Q/p-\alpha$ calc. ...	0.0	0.0	0.0	0.0	+0.2	+0.7	0.46
$Q/p-\beta$ calc. ...	-0.03	-0.09	0.00	-0.02	0.00	+0.24	+0.23

TABLE VIII.

Helium.

$$(Q=\alpha) \quad N_0=2.4, \quad V'=14.5.$$

$$(Q=\beta) \quad N_0=3.45, \quad V'=11.02.$$

z	60	50	40	30	20	[*] 10
Q/p	1.35	1.20	1.00	0.77	0.40	0.12
$Q/p-\alpha$ calc. ...	+0.01	0.00	-0.01	+0.02	-0.02	+0.046
$Q/p-\beta$ calc. ...	-0.03	-0.02	0.00	+0.03	+0.01	-0.03

10. It will be observed that, except in the cases of nitrogen and hydrogen, for which Townsend's figures agree peculiarly well with his theory, the assumption that $Q=\beta$ gives a better agreement between the observed and calculated numbers than the assumption that $Q=\alpha$; the difference is especially well marked for smaller values of z . Even in the case of the former assumption there is some systematic divergence in this region; a brief examination of the results which would be obtained, if it were not assumed that $f(x)$ is continuous, but the calculations carried through by examining in detail the history of the ions produced in each layer of the gas, shows that a divergence of the nature found might be caused by the error in this assumption. On the other hand, it is noticeable that the divergence is greater for gases which contain atoms of different kinds, a case which the theory has not attempted to consider. On the whole, it will be concluded universally that the tables afford no reason whatever for believing that the main physical assumptions on which the theory is based are not completely accurate. The correction of the slip in the mathematical work increases the confidence in the foundations of the theory.

The newly calculated values of V' are consistently lower, and the newly calculated value of N_0 consistently higher, than

those given by Townsend. On p. 30 of his book Townsend points out that the value of N_0 leads to an estimate of the radius of a molecule of the gas concerned and finds that the radii calculated by this method are somewhat smaller than those deduced by the ordinary methods of the dynamical theory of gases, based on observations of viscosity, &c. The increase in the value of N_0 due to the revised calculations leads to a nearer approximation between the values of the radius calculated by the two methods, but the correction is not sufficiently large to abolish the difference. It has been pointed out in § 3 that the error introduced by assumption (2) tends to make the values of N_0 , and therefore of the radius of the molecule, too small.

11. It will now be of interest to consider the other of the two alternative hypotheses mentioned in § 3, concerning the nature of the negative ion, and to discover in what way the theory will be altered by adopting it.

It is now supposed that the electron, which represents the negative ion immediately after its formation, can collect round it neutral molecules at subsequent collisions, and thus lose its power of ionizing by collision, except when the electric field is very much greater than that considered in the experiments under discussion. The simplest hypothesis which can be made in this direction, and that which seems on general grounds most likely to be true, is that, when an electron collides with a neutral molecule after travelling freely under the field a distance less than b and fails to ionize it, it adheres to that neutral molecule and forms what we shall call a "complex ion." Accordingly, on this hypothesis, an electron after it has once made a collision at which it fails to ionize the molecule with which it collides can never again ionize on collision in the conditions considered here. However it retains its charge and contributes to the current i in the same way as if it had remained a free electron.

12. Let $f(x)$ be still the number of free electrons entering from the positive side a layer of gas distant x from the positive electrode in one second; let $g(x)$ be the corresponding number of complex ions for the same layer. We shall now have

$$i/\epsilon = f(l) + g(l). \quad . \quad . \quad . \quad . \quad (19)$$

$g'(x)$ is the number of complex ions formed per second in the layer x . On our theory it must also be the number of the free electrons which in that layer collide for the first time with a neutral molecule, having previously travelled

freely a distance less than b . Accordingly all these free electrons have been produced between x and $x-b$. If the number of free electrons produced per second in any layer is q_x , since the probability that an electron produced at $x-y$ collides for the first time at x is $N e^{-Ny}$, where

$$g'(x) = \int_0^b q_{x-y} N e^{-Ny} dy. \quad (20)$$

q_x is not, as before, equal to $f'(x)$, for the value of $f(x)$ as we cross any layer is changed not only by the number of electrons produced there, but also by the number of electrons which disappear there, forming complex ions. In fact,

$$f'(x) = q_x - g'(x). \quad (21)$$

To determine q_x the considerations which lead to (8) are still valid, and we have

$$q_x = n_0 p + \alpha f(x-b). \quad (22)$$

The functions concerned here are, of course, discontinuous in just the same way as those considered previously. In order to proceed further in this direction it is again necessary to assume that they are continuous, and the conditions necessary to determine the integration constants will again be taken as those at $x=b$. If we again take

$$f(x) = A e^{\beta x} + B, \quad (23)$$

we get

$$\beta = \alpha e^{-\beta b} \left\{ 1 - \frac{N}{N+\beta} (1 - e^{-N+\beta \cdot b}) \right\}. \quad (24)$$

We shall have four integration constants, A , B , and two derived from integrating (20) to find $g(x)$. To determine these we have the four independent conditions at $x=b$,

$$f(b) = n_1 e^{-Nb} + \int_0^b n_0 p e^{-Ny} dy, \quad (25)$$

$$g(b) = n_1 + n_0 p b - f(b), \quad (26)$$

$$g'(b) = n_1 N e^{-Nb} + \int_0^b n_0 p N e^{-Ny} dy, \quad (27)$$

$$q_b = n_0 p + \alpha n_1.$$

The resulting equations are so complicated that no attempt has been made to apply them to experiments. But it may be noted that, in place of the simple exponential form (17) when $n_0=0$, we obtain

$$i_l \epsilon = P e^{\beta b} + Q l + R. \quad . \quad . \quad . \quad . \quad . \quad (17')$$

Accordingly, if this theory were correct, the curves obtained by Townsend should not have been accurately exponential. Sufficient measurements are not given to test this point, but the fact that consistent values of the exponential coefficient were obtained from different pairs of points, on the assumption that the curve was exponential, is some evidence against the second theory. But the distinction between the two theories can be best made by examining the calculated and observed relations between n_1 and n' and those constants in the equations which involve them. Townsend gives no values for n_1 , and hence this test cannot be applied. The experiments described in the next paper appear to provide a conclusive proof in favour of the first theory and against the second.

Summary.

1-3. The physical assumptions made in Townsend's theory of ionization by collision are analysed and discussed. It is pointed out that one of them is to the effect that the negative ion does not undergo any permanent change in its properties as a consequence of repeated collisions with neutral molecules. This assumption is contradictory to the older view of ionization by collision, according to which the negative ion, when first formed, is an electron, but subsequently becomes a "complex ion" by gathering round it neutral molecules.

4, 5. Townsend's mathematical argument, by which he applies these assumptions to certain cases of the discharge through gases, is sketched briefly.

6-8. It is pointed out that this argument contains an error. No attempt is made to arrive at completely accurate formulæ, but a nearer approximation is made.

8, 9. The new formulæ are applied to Townsend's measurements, and shown to agree with them better than those which he used.

10-12. Similar formulæ are briefly sketched based on the older view that a negative ion after collisions with neutral molecules becomes a complex ion. Townsend's experiments are not so well suited for distinguishing between the two

theories as those described in the following paper *. Further discussion of this point is, therefore, postponed until the account of that work is complete.

Leeds University,
Nov. 18, 1911.

Note added Feb. 10.

Mr. Bishop has recently (*Phys. Zeits.* xii. p. 1148, 1911) published an account of a very complete experimental test of the accuracy of Townsend's theory. His formula differs slightly from that of Townsend in the nature of the relation between α and the quantities N and V' , but it appears to me open to the same criticism as has been made in this paper, in that it does not reduce to the right form when l is less than b . The absence of a divergence between observed and calculated values is probably due to the fact that throughout his experiments l was much greater than b .

XXXVII. *Concerning the Thermal Expansion of Mercury, Remarks on a Paper by Callendar and Moss. By KARL SCHEEL and WILHELM HEUSE* †.

1. **A**BOUT a year ago Callendar and Moss ‡ published the results of a comprehensive investigation of the thermal expansion of mercury, in which they used the method of balanced hydrostatic tubes. The authors themselves state that there is a considerable difference between their results and those obtained by Chappuis § in the Bureau international des Poids et Mesures. They raise the objection against the measurements of Chappuis, who used the dilatometer method, that it is not allowable to calculate the cubical expansion of a body by multiplying its linear expansion measured in only one direction by 3, since the hereby assumed isotropy of the body is not certain.

One might consider perhaps that this objection is correct, if, as Callendar and Moss have done, only the results of Chappuis for the expansion of mercury are discussed. In reality, however, a proper opinion concerning the reliability

* To be published in the April number.

† Communicated by the Authors from the Physikalisch-Technischen Reichsanstalt.

‡ Hugh L. Callendar and Herbert Moss, *Phil. Trans. (A)* 211. pp. 1-32 (1911).

§ P. Chappuis, *Trav. et Mém. du Bureau international des Poids et Mesures*, xiii. C, 31 pp., 1903 (1907).

of his results can only be obtained when they have first been considered in connexion with his investigation of the expansion of water. And further, Callendar and Moss have neglected to bring into the discussion the comprehensive and pertinent results from the Reichsanstalt.

2. Chappuis by means of the weight thermometer method, and using a verre dur tube 1 metre long and 4 cm. in diameter, determined the expansion of mercury between 0° and 40° , and likewise in the neighbourhood of 100° , and the linear expansion of the tube by the comparator (Direct Method).

Further, he calculated through the use of the value found for 100° the course of the expansion between 0° and 100° by comparing the verre dur thermometer with a hydrogen thermometer (Indirect Method). The two methods give values which agree well, as will be seen below in the accompanying Table II.

3. The measurements of Chappuis are supported also by the fact that he determined by use of the same verre dur dilatometer the thermal expansion for water * between 0° and 40° and at 100° , and still further in that he also obtained the expansion of water between 0° and 40° by the use of a platinum-iridium dilatometer, whose linear expansion was obtained in the same way as that for the hard glass dilatometer.

The two investigations furnish excellent agreement, and seem already to weaken the objection of Callendar and Moss; for it is, indeed, hardly plausible that the two vessels of entirely different materials as used by Chappuis should be to the same degree ælotropic. Further, the Chappuis values also agree excellently with the results which Thiesen, Scheel, and Diesselhorst † and later Thiesen ‡ alone obtained between 0° and 40° and likewise at 100° for water by use of the balanced hydrostatic tubes. Besides this the Chappuis values are also in agreement with the results obtained in 1887 in the Bureau international by Thiesen § from the weight of a quartz-kilogram in water. All of these values relative to water are placed together in Table I. as variations from a mean value.

* P. Chappuis, *Trav. et Mém. du Bureau international des Poids et Mesures*, xii. D, 40 pp., 1904 (1907).

† M. Thiesen, K. Scheel und H. Diesselhorst, *Wiss. Abh. d. Phys.-Techn. Reichsanstalt*, iii. pp. 1-70 (1900).

‡ M. Thiesen, *ibid.* iv. pp. 1-32 (1904).

§ Benoit, *Trav. et Mém. du Bureau international des Poids et Mesures*, vii. p. 112 (1890).

TABLE I.

Specific volume of water with respect to that at 4°.

Temperature.	Mean Value.	VARIATIONS FROM THE MEAN VALUE $\times 10^6$.				
		Chappuis, Verre dur.	Chappuis, Platinum Iridium.	Thiesen, Scheel & Diesselhorst (absolute).	Thiesen (absolute).	Thiesen (by weighing).
0.....	1·000 132	-1	-1	0	...	+1
10.....	1·000 272	-1	-2	+1	...	+1
20.....	1·001 771	-3	-1	+2	...	+2
30.....	1·004 343	-4	-1	+3	...	+4
40.....	1·007 814	-6	0	+5	...	...
100.....	1·043 422	-11	...	...	+11	...

4. In the Reichsanstalt observations on the relative expansion of mercury in the Jena glasses 16^m and 59^m and also verre dur have been made between 0° and 100° by means of the weight thermometer method *. For the calculation of the absolute expansion of mercury use was made of the measurements of the linear expansion of one metre long rods of the same glasses which were placed on the comparator at 0°, 25°, 50°, 75°, and 100°. This calculation, however, was through cautiousness only applied to two dilatometers, those from the glasses 16^m and 59^m, since it was only with these two that there seemed to be sufficient guaranty that the dilatometer and glass rod were composed of the same material. Especially certain was the case of glass 59^m, since the dilatometer tube and capillary were furnished at almost the same time from the glass-works and so very probably originated from the same melting. For glass 16^m there still remains in this respect some doubt. On this point one of the conclusions drawn in the paper cited is in particular to be considered, namely, "that the Jena glass 16^m does not present sufficiently homogeneous properties for drawing any further conclusions." For this reason in the following Table II. for the expansion of mercury only those values obtained from the observations on the Jena glass 59^m dilatometer are given without reservation, while those results obtained from the dilatometer of glass 16^m are placed in parentheses.

By using the same method as Chappuis the mercury

* M. Thiesen, K. Scheel und L. Sell, *Wiss. Abh. d. Phys.-Techn. Reichsanstalt*, ii. pp. 73-184 (1895), especially pp. 160-163.

expansion between 0° and 100° was obtained by the comparison of thermometers. In this case too the values originating from glass 16^{III} are placed in parentheses in Table II.

5. Not only was the relative expansion of mercury determined by the use of the dilatometers mentioned in §4, but also that of water in glass. Thus one obtains for each dilatometer a value for the difference between the expansion for mercury and that of water, in the calculation of which the expansion of the glass is eliminated.

The expansion of water between 0° and 100° has already been determined by Thiesen * in the Reichsanstalt by the method of balanced hydrostatic tubes. If now the value found by him be combined with the above-mentioned dilatometer observations, the specific volume of mercury at 100° expressed in terms of that at 0° is obtained independent of the glass expansion as follows :—

From dilatometer 16 ^{III} No. 1	1·018 259
" " ,, No. 2	1·018 259
" " verre dur No. 3.	1·018 254
" " 59 ^{III}	1·018 267

Due to the excellent agreement of these separate determinations much weight must be attached to the mean value 1·018 260.

6. In the following Table II. the values for the expansion of mercury obtained in the Bureau international and in the Reichsanstalt are placed together in accordance to the foregoing discussion and as variations from a mean value.

TABLE II.

Temperature.	Mean Value.	VARIATIONS FROM THE MEAN VALUE $\times 10^6$.					
		Chappuis direct.	Chappuis indirect.	Thiesen, Scheel, and Sell.			Callendar and Moss.
				16 ^{III} .	59 ^{III} .	Absolute Thiesen.	
0.....	1·000 000	0	0	(0)	0	0	0
10.....	1·001 817	0	−1	(0)	0	...	−10
20.....	1·003 634	0	−2	(0)	+2	...	−18
30.....	1·005 453	−2	−2	(+ 1)	+3	...	−24
40.....	1·007 273	−3	−2	(+ 1)	+6	...	−29
100.....	1·018 257	−3	...	(−25)	−1	+3	−52

In the last column the observations of Callendar and Moss are added in the same form.

* *Loc. cit.*

The table shows not only the contradiction between the results of Callendar and Moss and the direct measurements of Chappuis, to which Callendar and Moss have already called attention, but shows also that the same contradiction is present with respect to Chappuis' observations by the indirect method, and likewise with all the measurements of the Reichsanstalt, all of which are in excellent agreement.

How this contradiction is to be explained must for the present remain undetermined. Still, so long as the results of Callendar and Moss are not confirmed from other sources it is scarcely allowable to use the comprehensive tables which they have given at the end of their publication, instead of those tables for the expansion of mercury between 0° and 100° which have been used up to the present.

7. Just lately Harlow *, at the suggestion of Callendar, has determined the cubical expansion of fused silica by the weight thermometer method, using mercury as the thermometric substance. He began the work with the same doubt which Callendar and Moss have raised, namely, whether it is allowable, with a claim to great accuracy, to calculate the cubical expansion of a body from the linear by the multiplication by 3. As the result of his observations on three dilatometers Harlow gives the mean cubical expansion coefficient of fused silica between 0° and 100° as $0.998 \cdot 10^{-6}$. On division by 3 one would obtain from this $0.33 \cdot 10^{-6}$ as the linear expansion coefficient. This value is in contradiction with all other known determinations for the linear expansion of fused quartz between 0° and 100° that have been obtained up to this time.

The following values for this coefficient were found by :—

Chappuis (1903 †) for a small cylinder of 10 mm. diameter prepared by himself	$0.50 \cdot 10^{-6}$
Scheel (1903 ‡) for a small cylinder 3.7 mm. in diameter from W. C. Heräus	$0.47 \cdot 10^{-6}$
Scheel (1903 ‡) for a small cylinder 7 mm. in diameter from W. C. Heräus	$0.46 \cdot 10^{-6}$
Scheel (1907 §) for a ring-shaped body from the firm Carl Zeiss, Jena	$0.51 \cdot 10^{-6}$
Holborn and Henning (1903) for a rod 2.9 mm. in diameter and 0.52 m. long from Heräus (mean expansion coefficient between 0° and 250°)	$0.48 \cdot 10^{-6}$

* F. J. Harlow, *Proc. Phys. Soc. London*, xxiv. pp. 30-39 (1912).

† P. Chappuis, *Verh. d. Naturf. Ges. Basel*, xvi. pp. 173-183 (1903).

‡ K. Scheel, *Verh. d. D. Phys. Ges.* v. pp. 119-123 (1903).

§ K. Scheel, *ibid.* ix. pp. 718-721 (1907).

|| L. Holborn and F. Henning, *Ann. d. Phys.* (4) x. pp. 446-448 (1903).

Now Harlow bases his calculation on the mean value $182.05 \cdot 10^{-6}$ for the thermal expansion coefficient of mercury between 0° and 100° as found by Callendar and Moss. If, however, the mean value $182.57 \cdot 10^{-6}$ obtained from the measurements of the Bureau international and the Reichsanstalt as given in Table II. is used instead, then the value $1.52 \cdot 10^{-6}$ will be obtained for the mean cubical expansion of fused silica between 0° and 100° , and from this through division by 3 the linear coefficient as $0.51 \cdot 10^{-6}$. This value is, however, in complete agreement with the direct measurements on very different specimens.

The observations of Harlow therefore do not force the assumption of the æolotropy of fused silica, but, on the other hand, indicate rather the presence of error in the measurements of Callendar and Moss.

Charlottenburg, January 1912.

XXXVIII. *Photographic Measurements of Pendent Drops.*

By ALLAN FERGUSON, *B.Sc. (Lond.)*, Assistant Lecturer in Physics in the University College of North Wales, Bangor*.

[Plate VIII.]

IN two interesting papers on Pendent Drops †, Mr. A. M. Worthington has shown how the surface tension of a fluid may be evaluated by tracing on paper the magnified image of a pendent drop of the fluid; if this outline be cut out of paper of uniform texture, the volume, position of the C.G., and the area of a meridional section of any given portion of the drop can be estimated, and from a knowledge of these quantities the surface tension of the fluid concerned may be calculated.

It seemed to the writer that this result might be obtained in a more convenient manner by photographing the pendent drop in such a way that the photograph should not only show the contour of the drop, but should also enable the distance from the "free" surface of the liquid employed to any point on the surface of the drop, to be measured; for the pressure-excess at any point P in the interior of the drop is given by

$$p = T \left(\frac{1}{R} + \frac{1}{R'} \right) = g\rho h,$$

* Communicated by Prof. E. Taylor Jones.

† Proc. Roy. Soc. June 1881; Phil. Mag. vol. xx, (1885).

Phil. Mag. S. 6. Vol. 23, No. 135, March 1911. 2 F

h being the vertical distance from the "free" surface to the point in question, R and R' the principal radii of curvature of the surface of the drop at any point of the surface in a horizontal plane passing through P . In particular, if the point P be taken at the vertex of the drop, we have

$$\frac{2T}{R} = g\rho h,$$

and measurements of h and R will serve to determine T .

The central idea of such a method possesses, of course, no novelty. In a lecture given at the Royal Institution*, Lord Kelvin showed a simple apparatus by means of which approximate measurements might be made, but in the calculation appended thereto the drop is treated as hemispherical, *i. e.* the two principal radii of curvature are treated as constant and equal in value at any point on the surface, a condition only approximately fulfilled when the drop is very small.

The main object of the present paper is to test the validity of various equations which may be obtained, empirically or otherwise, to fit the contour of the meridional section, especially in the neighbourhood of the vertex. For a knowledge of the equation to the section enables one to calculate the principal radii of curvature at any point, and hence to deduce the surface tension in terms of known quantities.

For small drops such an equation can be obtained by following a method first proposed by Laplace†, in which the differential equation of the meridional curve is integrated by assuming that a circle, of radius c , can be determined, whose ordinate, for a given abscissa, differs from that of the meridional curve by a small quantity whose square is negligible. The investigation of Laplace refers to the shape of the curved surface inside a cylindrical capillary tube, but, writing the equation of the surface in the form

$$\frac{1}{x} \frac{d}{dx} (x \sin \theta) = \frac{h-y}{a^2},$$

instead of

$$\frac{1}{x} \frac{d}{dx} (x \sin \theta) = \frac{h+y}{a^2}$$

* Proc. Roy. Inst. vol. xi. part iii.

† Laplace, *Mécanique Célest.* Supp. to Bk. x.; and Minchin, 'Hydrostatics,' Chap. viii.

where $a^2 \equiv T/g\rho$, and proceeding on similar lines, we obtain finally

$$y = c - \sqrt{c^2 - x^2} + \frac{c^3}{3a^2} \log_e \frac{2c}{c + \sqrt{c^2 - x^2}}.$$

The form of this resulting equation, however, containing, as it does, a mixture of algebraic and logarithmic terms, renders it somewhat unsuitable for numerical computations. A similar objection applies to the method devised by Prof. J. C. Adams* for the calculation of the forms of sessile drops of mercury,—a method which consists in “developing the increments of the coordinates in series proceeding according to ascending powers of the increment of the quantity chosen as the independent variable” †, and which, whilst of a high order of accuracy, is, in numerical work, laborious to a proportionate degree. It seemed, therefore, preferable to attempt to find an empirical equation which should, in the neighbourhood of the vertex, at any rate, fit sufficiently closely the outline of the meridional section of the drop.

An attempt to evaluate surface tensions in such a way seems all the more desirable, as it frees one from the necessity of troubling about that somewhat elusive quantity, the “angle of contact.” For liquids which wet the solid with which they are in contact, it is safe to assume the angle of contact to be zero, and for such liquids measurements of the height of rise of the liquid in capillary tubes are sufficiently exact; for other liquids, the determination of the angle of contact introduces an element of uncertainty, and the “method of ripples,” whilst avoiding the measurement of contact-angles, possesses the disadvantage that the equation for T is a cubic in λ , the term in λ^3 being the most important, so that a one-per-cent. error in the determination of the wave-length involves an error of approximately three-per-cent. in the value of the surface tension ‡.

The apparatus used and method pursued in this paper are as follows § :—

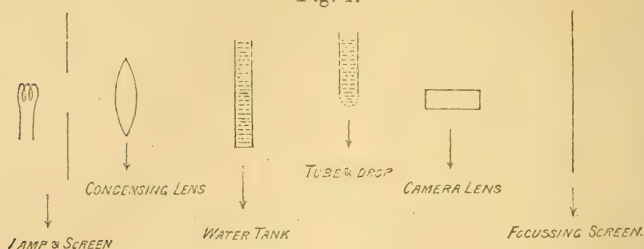
* Bashforth and Adams, ‘Capillary Action’ (Camb. Univ. Press, 1888).

† *Op. cit.* p. 15.

‡ Rayleigh, Scientific Papers, vol. iii. p. 389; and Watson, Physical Review, May 1901.

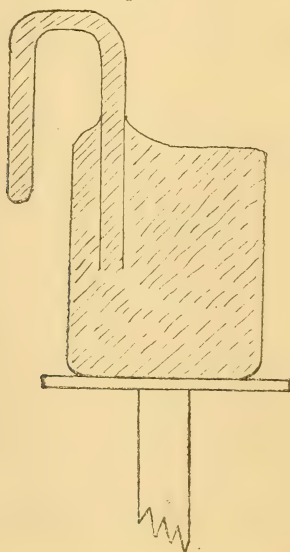
§ Cf. Worthington, Proc. Roy. Soc. June 1881.

Fig. 1.



The above diagram requires no comment, save that the water-tank—a glass cell with parallel sides—is used to prevent undue heating of the drop, and that the camera lens used is detached from the bellows of the camera, and fixed on an independent movable stand, thus permitting greater magnification.

Fig. 2.



The drop photographed is formed at the end of a siphon-tube standing vertically in a beaker brimful of the liquid employed. The end of the tube should be ground flat, and should be truly circular in section. The beaker itself stands on an adjustable table, by raising or lowering which the pressure in the drop can be varied and the curvature altered accordingly. Beaker, tube, and drop are photographed, and

the magnification is known, since the diameter of the tube on the photograph can be measured and compared with the actual diameter of the tube used.

After a few preliminary trials, a microscope objective was substituted for the camera lens, giving a much higher magnification. The drop itself now occupied almost the whole of the photographic plate, thus rendering two photographs necessary, one of the drop alone, another with a lower magnification showing both the drop and the horizontal surface of the fluid in the beaker.

After focussing the edge of the drop sharply on the screen, and before taking the photograph, a little fluid was run out of the siphon-tube by screwing up the adjustable table carrying the beaker. This ensured the cleanliness of the surface of the drop. The photograph under high magnification was then taken, the microscope objective removed and camera-lens substituted, the drop being now refocussed and the second photograph taken. The whole interval between exposing the surface of the drop to the air and taking the final photograph need not be much more than a minute, and the surface may fairly be assumed to be uncontaminated during this interval. The photographs so taken were measured by means of a travelling microscope provided with verniers reading to $\cdot 001$ centimetre, and capable of motion parallel to the axes of x and y ; a third motion, parallel to the z -axis, providing for the focussing of the microscope. Thus the coordinates of points on the meridional surface could be plotted out, and the coordinates of the vertex read off from the graph so obtained.

It is evident that if the vertex of the drop be taken as origin, the y -axis being drawn vertically upwards, the constant term in the equation to the curve will vanish, and, on account of the symmetry about the axis of y , only even powers of x will appear in the equation. The form of the equation will therefore be

$$y = bx^2 + cx^4 + \dots$$

In the tables given below, two types of equation were tried,—the parabolic form $y = bx^2$, and the biquadratic $y = bx^2 + cx^4$.

The exact equation to the surface of the drop is

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{(h-y)}{a^2} = A - By \text{ say, } \dots (\alpha)$$

where A and B are constants, h being the distance from the

"free" horizontal surface to the vertex of the drop. R_1 is the radius of curvature of the meridional curve at any point P whose coordinates are (x, y) , and R_2 , the second principal radius of curvature, is measured by the length of the normal at P to the meridional section intercepted between the point P and the axis of y . We have, therefore, where $\tan \phi = \frac{dy}{dx}$,

$$R_1 = \frac{(1+y_1^2)^{\frac{3}{2}}}{y_2}, \quad R_2 = \frac{x}{\sin \phi} = \frac{x(1+y_1^2)^{\frac{1}{2}}}{y_1}.$$

With these data, it is easy to see under what circumstances the parabolic equation $y = bx^2$ most nearly satisfies the requirements of equation (α). For we have

$$R_1 = \frac{(1+4b^2x^2)^{\frac{3}{2}}}{2b} = \frac{(1+4by)^{\frac{3}{2}}}{2b}$$

and

$$R_2 = \frac{(1+4by)^{\frac{1}{2}}}{2b}.$$

Hence

$$\begin{aligned} \frac{1}{R_1} + \frac{1}{R_2} &= 2b \left\{ \frac{2+4by}{(1+4by)^{\frac{3}{2}}} \right\} \\ &= (4b+8b^2y)(1-6by+30b^2y^2 \dots) \\ &= 4b-16b^2y(1-\frac{3}{2}by+\dots) \dots \dots (\beta) \\ &= A-By \end{aligned}$$

if by and the succeeding terms—which, it should be noted, are independent of the unit of length—are small compared with unity.

A similar result can be obtained for the biquadratic formula, $y = bx^2 + cx^4$. This equation provides a nearer approximation to the truth over a given range of the curve, as, for a given value of y , the ratio of the second to the third term in the expansion of $\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$ is sensibly greater than in the case of expansion (β) above.

Here also may be noted the effect of observational errors on the quantities computed. Thus, putting

$$z = \frac{1}{R_1} + \frac{1}{R_2} = 2b \left\{ \frac{2+4by}{(1+4by)^{\frac{3}{2}}} \right\}$$

and supposing z , b , and y to vary together, we have

$$\frac{\delta z}{z} = \frac{\delta b}{b} + \frac{2(b\delta y + y\delta b)}{1+2by} - \frac{6(b\delta y + y\delta b)}{1+4by}.$$

Suppose, *e. g.*, that b and y are measured to one per cent., so that

$$\delta b = .01 b, \quad \delta y = .01 y,$$

we have

$$\frac{\delta z}{z} = .01 + \frac{.04by}{1+2by} - \frac{.12by}{1+4by};$$

and, since, in general, by is small compared with unity, the percentage error in the computation of $\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$ is practically equal to the percentage error in the estimation of b .

The quantities actually measured are, of course, x and y ; and since

$$b = \frac{y}{x^2}$$

we have

$$\frac{\delta b}{b} = \frac{\delta y}{y} - 2 \frac{\delta x}{x},$$

showing that if x and y are subject to the same percentage error, the error in b has numerically the same value as the error in measurement of either x or y .

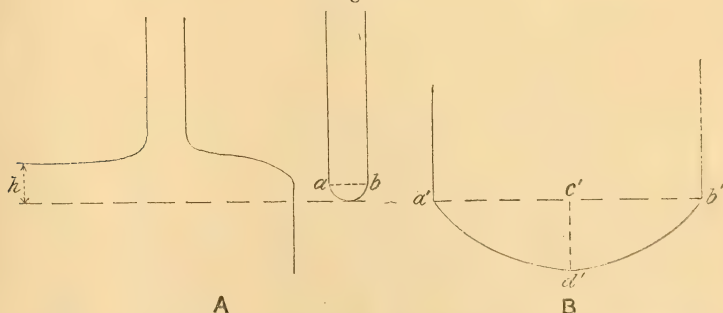
Finally, in the equation for the computation of T , viz. :—

$$T\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = g\rho h,$$

none of the above quantities involved are raised to a power which unduly multiplies the errors of observation.

The accompanying figure (fig. 3) shows on a reduced

Fig. 3.



scale the outlines of the two photographs of a drop actually measured; the figures relating thereto are given below. Figures A and B on Pl. VIII. (fig. 6) are reduced reproductions of the photographs, figures C and D on the

same plate showing a pendent drop formed under greater pressure.

Photograph A.

Fluid, distilled water. Temp. 11° C. Difference of level between horizontal surface of water in beaker and vertex of drop = 1.222 cm.

= h , say.

Diameter ab of tube on photo = 1.051 cm. True diameter, measured directly = .4459 cm.

$$\text{True value of } h = \frac{1.222 \times .4459}{1.051} \\ = .5186 \text{ cm.}$$

As a check on the value obtained from the photograph, a direct measurement of h was made by a travelling microscope, giving as a result

$$h = 3.418 - 2.902 = .516 \text{ cm.}$$

Photograph B. High magnification, showing drop alone. (Length-measurements in all cases given in centimetres. X and Y are actual readings of microscope, x and y the co-ordinates of points on the meridional surface referred to the vertex as origin.)

Extreme coordinates of drop

$$x = -3.606, y = 1.7155; \text{ and } x = 3.485, y = 1.6435.$$

Diameter of tube on photograph B = 7.166.

True diameter, measured directly = .4459.

$$\text{Magnification} = \frac{7.166}{.4459} = 16.07.$$

TABLE I.

Y.	X.	y .	x .	x^2 .	x^4 .	x^2y .	y' .	$y' - y$.
7.054	7.500	.2705	1.515	2.2950	5.2660	.6209	.2701	-.0004
6.985	7.700	.2015	1.315	1.7290	2.9890	.3483	.2029	+.0014
6.927	7.900	.1435	1.115	1.2430	1.5450	.1783	.1459	+.0024
6.882	8.100	.0985	.915	.8372	.7009	.0825	.0983	-.0002
6.844	8.300	.0605	.715	.5112	.2613	.0309	.0600	-.0005
6.814	8.500	.0305	.515	.2652	.0703	.0081	.0311	+.0006
6.797	8.700	.0135	.315	.0992	.0098	.0013	.0117	-.0018
6.787	8.900	.0035	.115	.0132	.0002	.0000	.0015	-.0020
6.786	9.100	.0025	+.085	.0072	.0001	.0000	.0008	-.0017
6.795	9.300	.0115	.285	.0812	.0066	.0009	.0095	-.0020
6.812	9.500	.0285	.485	.2352	.0552	.0067	.0276	-.0009
6.840	9.700	.0565	.685	.4692	.2202	.0265	.0551	-.0014
6.876	9.900	.0925	.885	.7832	.6134	.0724	.0919	-.0006
6.925	10.100	.1415	1.085	1.1760	1.3830	.1664	.1384	-.0031
6.977	10.300	.1935	1.285	1.6500	2.7230	.3193	.1936	+.0001
7.041	10.500	.2575	1.485	2.2040	4.8580	.5675	.2587	+.0012

$$\Sigma x^4 = 20.702.$$

$$\Sigma x^2 y = 2.4302$$

The value of the constant b in the equation $y = bx^2$ is obtained from the ordinary condition

$$\Sigma(y - bx^2)^2 = \text{minimum},$$

the condition for which, viz. :

$$\frac{\partial \Sigma}{\partial b} = 2\Sigma(y - bx^2)(-x^2) = 0$$

gives at once

$$b = \frac{\Sigma x^2 y}{\Sigma x^4} = \frac{2.4302}{20.702} = .1174.$$

Using the values of x in the fourth column and the equation $y' = .1174x^2$, the eighth column was computed. The ninth column shows the difference between the observed and calculated values of y , the difference in nearly every case falling within the limits of experimental error, as the verniers used read to .001 cm.

In deducing a value for the surface-tension from these measurements, it is to be remembered that all lengths have to be divided by the magnification to obtain their true values ; b , whose dimensions are those of the reciprocal of a length, must be multiplied by the magnification ; whilst by , which is of zero dimensions in length, requires no alteration.

At the vertex of the drop, the radius of curvature is given by

$$R = \frac{1}{y_2} = \frac{1}{2b},$$

and, therefore, in the equation

$$\frac{2T}{R} = g\rho h$$

we have T given by

$$T = \frac{g\rho h R}{2} = \frac{g\rho h}{4b}.$$

In every case, however, in which calculations were made using this formula, the values found for T were uniformly too low (about 70 dyne-cm.⁻¹). It is probable that this is due to the fact that the terms of importance in determining the value of b are rather too remote from the vertex ; to remove this difficulty, it will be necessary to use a higher magnification, in order to measure y -coordinates still nearer the vertex with a sufficiently high percentage accuracy.

But, using the figures given above, a sufficiently accurate estimate may be made by calculating the principal radii of

curvature at some point (x, y) in the neighbourhood of the important terms, and applying the relation

$$T\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = g\rho(h-y).$$

A numerical example will make the matter clear :—

Using the above data, take

$$x = 1.485$$

$$y = .2575$$

$$b = .1174$$

$$\text{Magnification} = \frac{7.166}{.4459}.$$

$$g = 981 \frac{\text{cm.}}{\text{sec}^2}$$

$$\rho = 1 \frac{\text{gm.}}{\text{c.c.}}$$

Then

$$\frac{1}{R_1} = \frac{2b}{(1 + 4b^2x^2)^{\frac{3}{2}}} = \frac{2 \times .1174 \times 7.166}{(1.1216)^{\frac{3}{2}} \times .4459} \\ = 3.175,$$

$$\frac{1}{R_2} = \frac{2b}{(1 + 4b^2x^2)^{\frac{3}{2}}} = \frac{2 \times .1174 \times 7.166}{(1.1216)^{\frac{3}{2}} \times .4459} \\ = 3.561,$$

$$\therefore \frac{1}{R_1} + \frac{1}{R_2} = 6.736.$$

$$\text{True value of } y = \frac{.2575 \times .4459}{7.166} = .0160,$$

$$\therefore h - y = .5186 - .0160 = .5026;$$

$$\therefore T = \frac{981 \times .5026}{6.736} = 73.2 \text{ dyne-cm.}^{-1}.$$

A similar calculation using the coordinates $x = 1.515$, $y = .2705$, gives

$$h - y = .5018$$

$$\frac{1}{R_1} + \frac{1}{R_2} = 6.709$$

and therefore $T = 73.4 \text{ dyne-cm.}^{-1}$ at a temperature of 11°C .

Turning now to the biquadratic equation $y = bx^2 + cx^4$, in computing b and c the same coordinates are used as in Table I. Some additional products are required and these are given in Table II.

TABLE II.

x^6 .	x^8 .	x^4y .	bx^2 .	cx^4 .	y' .	$y' - y$.
12.088	27.731	1.4240	.2710	.0020	.2690	-.0015
5.169	8.934	.6023	.2041	.0011	.2030	+.0015
1.921	2.387	.2217	.1468	.0006	.1462	+.0027
.587	.491	.0690	.0989	.0003	.0986	+.0001
.134	.068	.0158	.0604	.0001	.0603	-.0002
.019	.005	.0022	.0313	.00003	.0313	+.0008
.001		.0001	.0117		.0117	-.0018
.....			.0016		.0016	-.0029
.....			.0008		.0008	-.0017
.001			.0121		.0121	+.0006
.013	.003	.0016	.0278	.00002	.0278	-.0007
.103	.048	.0124	.0554	.0001	.0553	-.0012
.480	.376	.0567	.0925	.0002	.0923	-.0002
1.626	1.913	.1957	.1389	.0005	.1384	-.0031
4.492	7.415	.5270	.1948	.0010	.1938	+.0003
10.706	23.600	1.2510	.2602	.0018	.2584	+.0009

From the above table we have

$$\Sigma x^6 = 37.339, \quad \Sigma x^8 = 72.972, \quad \Sigma x^4 y = 4.3796.$$

To determine b and c , the principle of least squares gives

$$\Sigma (y - bx^2 - cx^4)^2 = \min.,$$

the condition for which, viz. :

$$\frac{\partial \Sigma}{\partial b} = \frac{\partial \Sigma}{\partial c} = 0,$$

gives as the normal equations for b and c

$$b \Sigma x^4 + c \Sigma x^6 = \Sigma x^2 y$$

$$b \Sigma x^6 + c \Sigma x^8 = \Sigma x^4 y.$$

Substituting the numerical values, and solving,

$$b = .1181, \quad c = -.000375,$$

giving as the equation to the meridian curve over the portion considered

$$y = .1181x^2 - .000375x^4.$$

Using the same values of x as in Table I. the R.H.S. of this equation was evaluated as shown in Table II., the last column of which shows, as before, the difference between the observed and computed values of y . It will be noticed that, whilst the deviations are of the same order as those corresponding to the parabolic formula, they are much more

evenly distributed with regard to sign, 7 being positive and 9 negative, while in Table I. 5 are positive and 11 negative.

To compute a value for T , taking as coordinates

$$x = 1.515, \quad y = .2690,$$

$$y_1 = 2bx + 4cx^3$$

$$= .3526,$$

$$\therefore 1 + y_1^2 = 1.1243.$$

$$y_2 = 2b + 12cx^2$$

$$= .2352,$$

$$\therefore \frac{1}{R_1} = \frac{.2352}{(1.1243)^{\frac{3}{2}}} \times \frac{7.166}{.4459} = 3.172,$$

$$\frac{1}{R_2} = \frac{.3526}{1.515(1.1243)^{\frac{3}{2}}} \times \frac{7.166}{.4459} = 3.527,$$

$$\therefore \frac{1}{R_1} + \frac{1}{R_2} = 6.699.$$

$$\text{True value of } y = \frac{.2690 \times .4459}{7.166} = .0167,$$

$$\therefore h - y = .5186 - .0167 = .5019.$$

$$\text{Finally, } T = \frac{\rho \times .5019}{6.699} = 73.5 \frac{\text{dynes}}{\text{cm.}}.$$

The mean value for the surface-tension of water at 11°C . is therefore $73.4 \frac{\text{dynes}}{\text{cm.}}$. The value as given by other experimenters varies with the method of experiment adopted, but taking the formula in Poynting & Thomson's 'Properties of Matter' as a standard of reference, viz. :

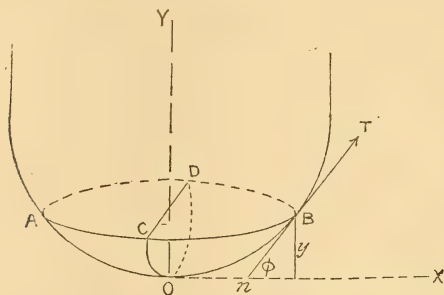
$$T_t = 75.8 - .152 t,$$

this gives T_{11} as $74.1 \text{ dyne-cm.}^{-1}$, and the two numbers are in agreement to within one per cent.

The above results have been selected as typical from the examination of a number of photographs, all of which gave results very similar to those detailed above. Amongst the photographs measured it was, as might be expected, found that the parabolic formula could be best applied when the drop was fairly, but not too flat in outline; as a rough criterion, the ratio of the extreme breadth to the extreme depth of the drop ($a'b' \div c'd'$ in fig. 3, Δ) should be about 4 : 1 to give convenient measurements.

It is worth noting that the assumption of a parabolic section permits of the equations of equilibrium of the part of the drop in the neighbourhood of the vertex being put into a very simple form.

Fig. 4.



Let the coordinates of B be (x, y) . Draw the tangent at B, and consider the equilibrium of the portion of the drop below the horizontal section ACBD.

Resolving vertically, we have, if P be the atmospheric pressure, h the distance from O to the "free," horizontal surface of the liquid, and V the volume of the drop below the horizontal plane ACBD,

$$2\pi xT \sin \phi + P \cdot \pi x^2 = V\rho g + [P + g\rho(h-y)] \cdot \pi x^2,$$

or

$$2xT \sin \phi = \frac{g\rho y^2}{2b} + g\rho(h-y)x^2, \quad . \quad . \quad . \quad (i.)$$

since

$$V = \frac{\pi y^2}{2b}.$$

Considering the equilibrium of the portion BCDO, and resolving horizontally, we have, if s be the length of the parabolic arc DOC,

$$Ts + P \times \frac{4}{3}xy = 2x \cdot T \cos \phi + \frac{4}{3}(P + g\rho h)xy - \frac{4}{5}g\rho xy^2,$$

or

$$2xT \cos \phi - Ts = \frac{4}{5}g\rho xy^2 - \frac{4}{3}g\rho hxy \quad . \quad . \quad . \quad (ii.)$$

And, eliminating $g\rho h$ between (i.) and (ii.), we obtain on

reduction

$$T \left\{ 2x \cos \phi + \frac{8}{3} y \sin \phi - s \right\} = \frac{2}{15} g \rho x y^2,$$

where $\tan \phi \equiv \frac{dy}{dx} = 2bx$. This equation affords a means for estimating T by measurements made on the drop alone, a method which may prove useful in certain cases (*e. g.* a pendent drop of a molten metal) where it is experimentally impracticable to make measurements of h . It is to be remembered, however, that the coefficient of T is small, and is obtained as a difference, so that reliable results would require somewhat close measurement and a high percentage accuracy in the experimental observations.

To sum up. The above results would seem to point to the following conclusions :—

(1) Over a definite portion of the drop near the vertex, the outline may be represented by a parabolic or biquadratic equation.

(2) The constants of this equation can be readily determined, thus allowing of an evaluation of the surface-tension independently of any knowledge of the angle of contact.

(3) By forming the pendent drop in a rectangular glass tank or cell filled with another fluid, interfacial tensions can be measured in a similar manner.

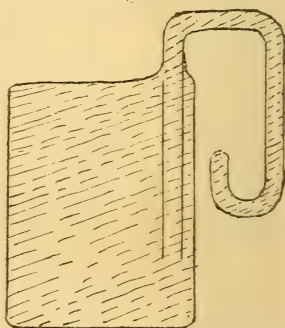
(4) By turning up the end of the siphon-tube in the manner shown, the phenomena attendant on the formation of sessile drops can be similarly studied.

(5) Granted sufficient experimental accuracy, determinations of T can be made from measurements carried out on the drop alone.

The writer trusts, in a subsequent communication, to detail results dealing with the above points.

University College of North Wales,
Bangor.
Oct., 1911.

Fig. 5.



XXXIX. *On Departures from Fresnel's Laws of Reflexion.**By* Lord RAYLEIGH, *O.M., F.R.S.**

IN the summer of 1907, in connexion with my experiments upon reflexion from glass at the polarizing angle †, I made observations also upon the diamond, a subject in which Kelvin had expressed an interest. It was known from the work of Jamin and others that the polarization of light reflected from this substance is very far from complete at any angle of incidence, and my first experiments were directed to ascertain whether this irregularity could be plausibly attributed to superficial films of foreign matter, such as so greatly influence the corresponding phenomena in the case of water ‡. The arrangements were of the simplest. The light from a paraffin flame seen edgewise was reflected from the diamond and examined with a nicol, the angle being varied until the reflexion was a minimum.

In one important respect the diamond offers advantages, in comparison, for instance, with glass, where the surface is the field of rapid chemical changes due presumably to atmospheric influences. On the other hand, the smallness of the available surfaces is an inconvenience which, however, is less felt than it would be were high precision necessary in the measurements. Two diamonds were employed—one, kindly lent me by Sir W. Crookes, mounted at the end of a bar of lead, the other belonging to a lady's ring. No particular difference in behaviour revealed itself.

The results of repeated observations seemed to leave it improbable that any process of cleaning would do more than reduce the reflexion at the polarizing angle. Potent chemicals, such as hot chromic acid, may be employed, but there is usually a little difficulty in the subsequent preparation. After copious rinsing, at first under the tap and then with distilled water from a wash-bottle, the question arises how to dry the surface. Any ordinary wiping may be expected to nullify the chemical treatment; but if drops are allowed to dry on, the effect is usually bad. Sometimes it is possible to shake the drops away sufficiently. After a successful operation of this sort wiping with an ordinarily clean cloth usually increases the minimum reflexion, and of course a touch with the finger, however prepared, is much worse. As the result of numerous trials I got the impression that the reflexion could not be reduced below a certain standard

* Communicated by the Author.

† Phil. Mag. vol. xvi. p. 444 (1908); Scientific Papers, vol. v. p. 489.

‡ Phil. Mag. vol. xxxiii. p. 1 (1892); Scientific Papers, vol. iii. p. 496.

which left the flame still easily visible. Rotation of the diamond surface in its own plane seemed to be without effect.

During the last few months I have resumed these observations, using the same diamonds, but with such additions to the apparatus as are necessary for obtaining measures of the residual reflexion. Besides the polarizing nicol, there is required a quarter-wave mica plate and an analysing nicol, to be traversed successively by the light after reflexion, as described in my former papers. The analysing nicol is set alternately at angles $\beta = \pm 45^\circ$. At each of these angles extinction may be obtained by a suitable rotation of the polarizing nicol; and the observation consists in determining the angle $\alpha' - \alpha$ between the two positions. Jamin's k , representing the ratio of reflected amplitudes for the two principal planes when light incident at the angle $\tan^{-1}\mu$ is polarized at 45° to these planes, is equal to $\tan \frac{1}{2}(\alpha' - \alpha)$. The sign of $\alpha' - \alpha$ is reversed when the mica is rotated through a right-angle, and the absolute sign of k must be found independently.

Wiped with an ordinarily clean cloth, the diamond gave at first $\alpha' - \alpha = 2^\circ.3$. By various treatments this angle could be much reduced. There was no difficulty in getting down to 1° . On the whole the best results were obtained when the surface was finally wiped, or rather pressed repeatedly, upon sheet asbestos which had been ignited a few minutes earlier in the blowpipe flame; but they were not very consistent. The lowest reading was $0^\circ.4$; and we may, I think, conclude that with a clean surface $\alpha' - \alpha$ would not exceed $0^\circ.5$. No more than in the case of glass, did the effect seem sensitive to moisture, no appreciable difference being observable when chemically dried air played upon the surface. It is impossible to attain absolute certainty, but my impression is that the angle cannot be reduced much further. So long as it exceeds a few tenths of a degree, the paraffin flame is quite adequate as a source of light.

If we take for diamond $\alpha' - \alpha = 30'$, we get

$$k = \tan \frac{1}{2}(\alpha' - \alpha) = .0044.$$

Jamin's value for k is .019, corresponding more nearly with what I found for a merely wiped surface.

Similar observations have been made upon the face of a small dispersing prism which has been in my possession some 45 years. When first examined, it gave $\alpha' - \alpha = 9^\circ$, or thereabouts. Treatment with rouge on a piece of calico, stretched over a glass plate, soon reduced the angle to 4° or 3° , but

further progress seemed more difficult. Comparisons were rendered somewhat uncertain by the fact that different parts of the surface gave varying numbers. After a good deal of rubbing, $\alpha' - \alpha$ was reduced to such figures as 2° , on one occasion apparently to $1\frac{1}{2}^\circ$. Sometimes the readings were taken without touching the surface after removal from the rouge, at others the face was breathed upon and wiped. In general, the latter treatment seemed to increase the angle. Strong sulphuric acid was also tried, but without advantage, as also putty-powder in place of or in addition to rouge. The behaviour did not appear to be sensitive to moisture, or to alter appreciably when the surface stood for a few days after treatment.

Thinking that possibly changes due to atmospheric influences might in nearly half a century have penetrated somewhat deeply into the glass, I re-ground and polished (sufficiently for the purpose) one of the originally unpolished faces of the prism, but failed even with this surface to reduce $\alpha' - \alpha$ below 2° . As in the case of the diamond, it is impossible to prove absolutely that $\alpha' - \alpha$ cannot be reduced to zero, but after repeated trials I had to despair of doing so. It may be well to record that the refractive index of the glass for yellow rays is 1.680.

These results, in which k (presumably positive) remained large in spite of all treatment, contrast remarkably with those formerly obtained on less refractive glasses, one of which, however, appeared to contain lead. It was then found that by re-polishing it was possible to carry k down to zero and to the negative side, somewhat as in the observations upon water it was possibly to convert the negative k of ordinary (greasy) water into one with a small positive value, when the surface was purified to the utmost.

There is another departure from Fresnel's laws which is observed when a piece of plate glass is immersed in a liquid of equal index *. Under such circumstances the reflexion ought to vanish.

The liquid may consist of benzole and bisulphide of carbon, of which the first is less and the second more refractive than the glass. If the adjustment is for the yellow, more benzole or a higher temperature will take the ray of equal index towards the blue and *vice versa*. "For a closer examination the plate was roughened behind (to destroy the second reflexion), and

* "On the Existence of Reflexion when the relative Refractive Index is Unity," Brit. Assoc. Report, p. 585 (1887); Scientific Papers, vol. iii, p. 15.

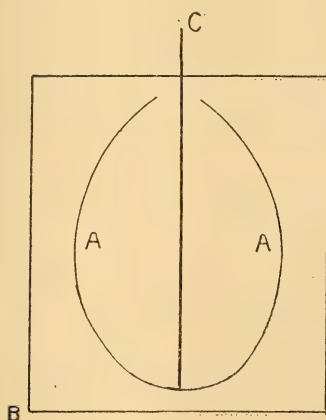
was mounted in a bottle prism in such a manner that the incidence could be rendered grazing. When the adjustment of indices was for the yellow, the appearances observed were as follows: if the incidence is pretty oblique, the reflexion is total for the violet and blue; scanty, but not evanescent, for the yellow; more copious again in the red. As the incidence becomes more and more nearly grazing, the region of total reflexion advances from the blue end closer and closer upon the ray of equal index, and ultimately there is a very sharp transition between this region and the band which now looks very dark. On the other side the reflexion revives, but more gradually, and becomes very copious in the orange and red. On this side the reflexion is not technically total. If the prism be now turned so that the angle of incidence is moderate, it is found that, in spite of the equality of index for the most luminous part of the spectrum, there is a pretty strong reflexion of a candle-flame, and apparently without colour. With the aid of sunlight it was proved that in the reflexion at moderate incidences there was no marked chromatic selection, and in all probability the blackness of the band in the yellow at grazing incidences is a matter of contrast only. Indeed, calculation shows that according to Fresnel's formulæ, the reflexion would be nearly insensible for all parts of the spectrum when the index is adjusted for the yellow." It was further shown that the reflexion could be reduced, but not destroyed, by re-polishing or treatment of the surface with hydrofluoric acid.

I have lately thought it desirable to return to these experiments under the impression that formerly I may not have been sufficiently alive to the irregular behaviour of glass surfaces which are in contact with the atmosphere. I wished also to be able to observe the transmitted as well as the reflected light. A cell was prepared from a tin-plate cylinder 3 inches long and 2 inches in diameter by closing the ends with glass plates cemented on with glue and treacle. Within was the glass plate to be experimented on, of similar dimensions as to be nearly a fit. A hole in the cylindrical wall allowed the liquid to be poured in and out. Although the plate looked good and had been well wiped, I was unable to reproduce the old effects; or, for a time, even to satisfy myself that I could attain the right composition of the liquid. Afterwards a clue was found in the spectra formed by the edges of the plate (acting as prisms) when the cell was slewed round. The subject of observation was a candle placed at a moderate distance. When the adjustment of indices is correct for any ray, the corresponding part of the spectrum

is seen in the same direction as is the undispersed candle-flame by rays which have passed outside the plate. Either spectrum may be used, but the best for the purpose is that formed by the edge nearer the eye. There was now no difficulty in adjusting the index for the yellow ray, and the old effects ought to have manifested themselves; but they did not. The reflected image showed little deficiency in the yellow, although the incidence was nearly grazing, while at moderate angles it was fairly bright and without colour. This considerable departure from Fresnel's laws could only be attributed to a not very thin superficial modification of the glass rendering it optically different from the interior.

In order to allow of the more easy removal and replacement of the plate under examination, an altered arrangement was introduced, in which the aperture at the top of the cell extended over the whole length. The general dimensions being the same as before, the body of the cell was formed by bending round a rectangular piece of tin-plate A (fig. 1) and securing the ends, to which the glass faces B were to be

Fig. 1.



cemented, by enveloping copper wire. The plate C could then be removed for cleaning or polishing without breaking a joint. In emptying the cell it is necessary to employ a large funnel, as the liquid pours badly.

The plate tried behaved much as the one just spoken of. In the reflected light, whether at moderate angles or nearly grazing, the yellow-green ray of equal index did not appear to be missing. A line or rather band of polish, by putty-powder applied with the finger, showed a great alteration.

Near grazing there was now a dark band in the spectrum of the reflected light as formerly described, and the effect was intensified when the polish affected *both* faces. In the transmitted light the spectrum was shorn of blue and green, the limit coming down as grazing is approached—a consequence of the total reflexion of certain rays which then sets in. But at incidences far removed from grazing the place of equal index in the spectrum of the reflected light showed little weakening. A few days' standing (after

polishing) in the air did not appear to alter the behaviour materially. On the same plate other bands were treated with hydrofluoric acid—commercial acid diluted to one-third. This seemed more effective than the putty-powder. At about 15° off grazing the spectrum of the reflected light still showed some weakening in the ray of equal index.

In the cell with parallel faces it is not possible to reduce the angle of incidence (reckoned from the normal) sufficiently, a circumstance which led me to revert to the 60° bottle-prism. A strip of glass half an inch wide could be inserted through the neck, and this width suffices for the observation of the reflected light. But I experienced some trouble in finding the light until I had made a calculation of the angles concerned. Supposing the plane of the reflecting surface to be parallel to the base of the prism, let us call the angle of incidence upon it χ , and let θ , ϕ be the angles which the ray makes with the normal to the faces, externally and internally, measured in each case *towards* the refracting angle of the prism. Then

$$\chi = 60^\circ - \phi, \quad \phi = \sin^{-1} \left(\frac{2}{3} \sin \theta \right).$$

The smallest χ occurs when $\theta = 90^\circ$, in which case $\chi = 18^\circ 10'$. This value cannot be actually attained, since the emergence would be grazing. If $\chi = 90^\circ$, giving grazing reflexion, $\theta = -48^\circ 36'$. Again, if $\theta = 0$, $\chi = 60^\circ$; and if $\chi = 45^\circ$, $\theta = 22^\circ 51'$. We can thus deal with all kinds of reflexion from $\chi = 90^\circ$ down to nearly 18° , and this suffices for the purpose.

The strip employed was of plate glass and was ground upon the back surface. The front reflecting face was treated for about 30s with hydrofluoric acid. It was now easy to trace the effects all the way from grazing incidence down to an incidence of 45° or less. The ray of equal index was in the yellow-green, as was apparent at once from the spectrum of the reflected light near grazing. There was a very dark band in this region, and total reflexion reaching nearly down to it from the blue end. The light was from a paraffin flame, at a distance of about two feet, seen edge-ways. As grazing incidence is departed from, the flame continues at first to show a purple colour, and the spectrum shows a weakened, but not totally absent, green. As the angle of incidence χ still further decreases, the reflected light weakens both in intensity and colour. When $\chi = 45^\circ$, or thereabouts, the light was weak and the colour imperceptible. After two further treatments with hydrofluoric acid and immediate examination, the light seemed further

diminished, but it remained bright enough to allow the absence of colour to be ascertained, especially when the lamp was temporarily brought nearer. An ordinary candle-flame at the same (2 feet) distance was easily visible.

In order to allow the use of the stopper, the strip was removed from the bottle-prism when the observations were concluded, and it stood for four days exposed to the atmosphere. On re-examination it seemed that the reflexion at $\chi=45^\circ$ had sensibly increased, a conclusion confirmed by a fresh treatment with hydrofluoric acid.

It remains to consider the theoretical bearing of the two anomalies which manifest themselves (i.) at the polarizing angle, and (ii.) at other angles when both media have the same index, at any rate for a particular ray. Evidently the cause may lie in a skin due either to contamination or to the inevitable differences which must occur in the neighbourhood of the surface of a solid or fluid body. Such a skin would explain both anomalies and is certainly a part of the true explanation, but it remains doubtful whether it accounts for everything. Under these circumstances it seems worth while to inquire what would be the effect of less simple boundary conditions than those which lead to Fresnel's formulæ.

On the electromagnetic theory, if θ, θ_1 are respectively the angles of incidence and refraction, the ratio of the reflected to the incident vibration is, for the two principal polarizations,

$$\frac{\tan \theta_1 / \tan \theta - \mu / \mu_1}{\tan \theta_1 / \tan \theta + \mu / \mu_1} \quad \dots \quad (A)$$

and

$$\frac{\tan \theta_1 / \tan \theta - K / K_1}{\tan \theta_1 / \tan \theta + K / K_1} \quad \dots \quad (B)$$

in which K, μ are the electric and magnetic constants for the first medium, K_1, μ_1 for the second*. The relation between θ and θ_1 is

$$K_1 \mu_1 : K \mu = \sin^2 \theta : \sin^2 \theta_1. \quad \dots \quad (C)$$

It is evident that mere absence of refraction will not secure the evanescence of reflexion for both polarizations, unless we assume both $\mu_1 = \mu$ and $K_1 = K$. In the usual theory μ_1 is supposed equal to μ in all cases. (A) then identifies itself with Fresnel's sine-formula, and (B) with the tangent-formula, and both vanish when $K_1 = K$ corresponding to no

* "On the Electromagnetic Theory of Light," *Phil. Mag.* vol. xii. p. 81 (1881); *Scientific Papers*, vol. i. p. 521.

refraction. Further, (B) vanishes at the Brewsterian angle, even though there be refraction. A slight departure from these laws would easily be accounted for by a difference between μ_1 and μ , such as in fact occurs in some degree (diamagnetism). But the effect of such a departure is not to interfere with the complete evanescence of (B), but merely to displace the angle at which it occurs from the Brewsterian value. If $\mu_1/\mu = 1 + h$, where h is small, calculation shows that the angle of complete polarization is changed by the amount

$$\delta\theta = -\frac{hn^3}{(n^2+1)(n^2-1)}, \quad \dots \quad (D)$$

n being the refractive index. The failure of the diamond and dense glass to polarize completely at some angle of incidence is not to be explained in this way.

As I formerly suggested, the anomalies may perhaps be connected with the fact that one at least of the media is *dispersive*. A good deal depends upon the cause of the dispersion. In the case of a stretched string, vibrating transversely and endowed with a moderate amount of stiffness, the boundary conditions would certainly be such as would entail a reflexion in spite of equal velocity of wave-propagation. All optical dispersion is now supposed to be of the same nature as what used to be called *anomalous* dispersion, *i. e.* to be due to resonances lying beyond the visible range. In the simplest form of this theory, as given by Maxwell* and Sellmeier, the resonating bodies take their motion from those parts of the æther with which they are directly connected, but they do not influence one another. In such a case the boundary conditions involve merely the continuity of the displacement and its first derivative, and no complication ensues. When there is no refraction, there is also no reflexion. By introducing a mutual reaction between the resonators, and probably in other ways, it would be possible to modify the situation in such a manner that the boundary conditions would involve higher derivatives, as in the case of the stiff string, and thus to allow reflexion in spite of equality of wave-velocities for a given ray.

P.S. Jan. 15.—Some later observations upon a surface of *fused quartz* are of interest. The plate, prepared by Messrs. Hilger, was $\frac{1}{2}$ inch square, and the surfaces were inclined at a few degrees so as to separate the reflexions.

* Cambridge Calendar for 1869. See Phil. Mag. vol. xlviii. p. 151 (1899); Scientific Papers, vol. iv. p. 413.

From these surfaces the reflexion at the polarizing angle *sensibly disappears*. The image of the paraffin flame could be quenched by the operation of the polarizing nicol alone. When the quarter wave-plate and analysing nicol were introduced, α' and α could not be distinguished, the difference probably not exceeding 0.5° , *i. e.* 3 minutes of angle.

In order to examine the reflexion when the quartz was in contact with a liquid of equal index, I had to mix alcohol with the benzole. The behaviour was then much the same as with glass of which the surface had been renewed by hydrofluoric acid. No precise measures could be taken, but the reflexion at 45° incidence seemed less than from the glass, though still easily visible. In spite of repeated trials with intermediate cleanings, it was difficult to feel sure that the residual effect might not be due to foreign matter, the more as differences could sometimes be detected between various parts of the surface*. Even if the surface could be regarded as clean on immersion, there is no certainty that a capillary film of some sort might not be deposited upon it from the liquid. The cause of the small residual reflexion must remain for the present an open question.

XL. *The Ranges of the α Particles from Uranium.* By H. GEIGER, *Ph.D., Lecturer in Physics*, and J. M. NUTTALL, *B.Sc., Graduate Scholar, University of Manchester*†.

IN connexion with a re-determination of the ranges of the α particles of a number of radioactive products, we have pointed out in a previous paper‡ that there exists a quantitative relation between the range of an α particle and the transformation constant of the product from which it arises. This was arrived at by plotting the logarithms of the transformation constants against the logarithms of the ranges of the respective products. In this way approximately straight lines were obtained passing through the points representing the products of the Uranium-Radium and of the Actinium series. No details have yet been given for the Thorium series on account of insufficient data.

A certain difficulty remained as regards uranium. As Boltwood§ has shown, this substance emits two α particles for one

* At the top of the plate, where it was attached to a handle, a slight invasion of gelatine (used as a cement) gave rise to a copious reflexion; but this film was easily visible in the air.

† Communicated by Prof. E. Rutherford, F.R.S.

‡ H. Geiger and J. M. Nuttall, *Phil. Mag.* vol. xxii. p. 613 (1911).

§ B. B. Boltwood, *Amer. Journ. of Sci.* vol. xxv. p. 269 (1908).

from each of the subsequent products, and this has been confirmed by the scintillation method by Geiger and Rutherford*. This may be ascribed to the existence of two successive α -ray products, or to the simultaneous emission of two α particles in the disintegration of each atom. The latter hypothesis is excluded by the experiments of Marsden and Barratt †, who found no evidence that two α particles were emitted simultaneously. It seems therefore probable that there exist two successive products each of long period which cannot be separated by ordinary chemical methods. To settle definitely whether this is the case, experiments have been made which will be described in this paper, to determine accurately the ionization curve of the α particles from a very thin film of uranium. For purpose of comparison, curves were taken under exactly the same conditions for films of ionium and polonium. Assuming that there are present in uranium two α -ray products whose difference of range is at least one millimetre (which means that the two periods differ by about a factor 10), this would affect the ionization curve to such an extent that it would be distinguishable from the ionization curves of simple α -ray products like ionium or polonium.

The method of determining the ionization curve of an α particle, originally devised by Bragg ‡, consists in the measurement of the ionization produced by a parallel pencil of α rays in a shallow ionization vessel placed at different distances from the source. This method can easily be applied if the material can be obtained as a very thin film of high activity. Since, however, uranium shows only a very low activity it was necessary to modify the original arrangement of Bragg. In the first place, it seemed advisable to make the dimensions of the apparatus as large as possible to enable the use of films of very large area. In the second place, it appeared advantageous to combine the ionization vessel and the measuring instrument by using an electroscope which has a small capacity and allows the accurate measurement of very minute ionization currents.

The arrangement used in the experiments will be seen from fig. 1. The main part of the apparatus consisted of two large bell-jars AA and BB, separated by a brass plate CC. A large number of holes—about 250—each 3.7 mm. in diameter and 8 mm. high, forming a circular “grid” of

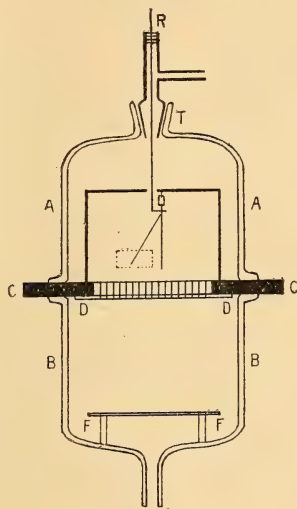
* H. Geiger and E. Rutherford, *Phil. Mag.* vol. xx. p. 691 (1910).

† E. Marsden and T. Barratt, *Proc. Phys. Soc.* vol. xxiii. p. 367 (1911).

‡ W. H. Bragg and R. D. Kleeman, *Phil. Mag.* vol. viii. p. 726 (1904); vol. x. p. 318 (1905).

10 cm. diameter, were drilled through the brass plate CC. An exactly similar but much thinner brass plate DD could be screwed on to the lower side of the plate CC. Between

Fig. 1.



these two plates a thin and uniform sheet of mica of stopping power equivalent to 8 mm. of air was placed and fixed down air-tight. On account of its position between the metal grids the mica was secured against breakage, and was then easily able to withstand an excess of 20 cm. pressure from either side; this difference of pressure was frequently necessary in the course of the experiments. The lower bell-jar BB contained the active film FF at a distance of 9.8 cm. from the mica. On account of the metal grid only the α particles emitted at angles less than 20 degrees to the normal could pass through the mica into the upper bell-jar which contained the electroscope. The latter was cylindrical in shape and was 8 cm. high and 10.5 cm. in diameter. It could be charged from outside through the wire R which could be rotated by means of the ground-glass joint T.

In the experiments the upper bell-jar was first completely exhausted and then filled with hydrogen up to a pressure of about 9 cm. of mercury. The use of hydrogen is preferable to air since, according to Taylor* and others, the rise of the ionization curve is more pronounced in the former gas than

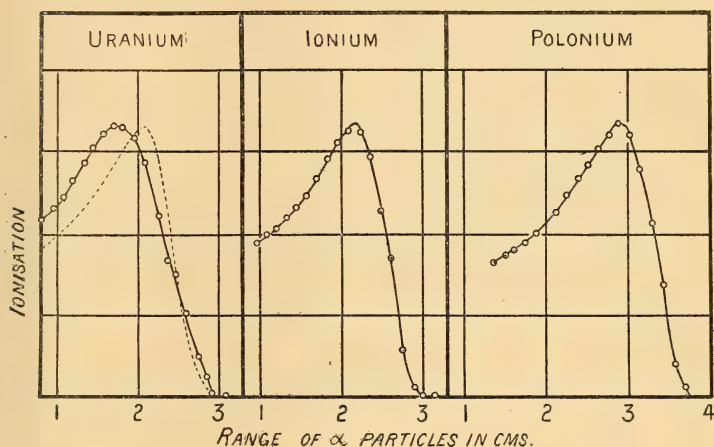
* T. S. Taylor, *Phil. Mag.* vol. xviii. p. 604 (1909); vol. xxi. p. 571 (1911).

in the latter. When filled with hydrogen to 9 cm. pressure the depth of the ionization vessel corresponded to 2.5 mm. of air at atmospheric pressure, since the α particles had to travel on an average through about 8.5 cm. in the electroscope before they were stopped by the upper plate. The ionization at different parts of the range of the α particles could be measured by varying the pressure in the lower bell-jar. When the latter was completely exhausted the range of the α particles on entering the electroscope was only diminished by about 8 mm., the distance corresponding to the stopping power of the mica. When the pressure in the lower vessel exceeded 25 cm., the α particles were completely stopped and the ionization then observed in the electroscope was due to the natural effect only. By measuring the ionization for different pressures in BB between the above limits a complete ionization curve was obtained. A film of uranium which contained .4 mgr. per square cm. gave an easily measurable effect—about .3 div./min. corrected for natural leak.

The films used in the experiments were prepared in the following way. A round glass plate of about 15 cm. diameter was carefully ground on one side by means of very fine emery. Pure uranium oxide which was well powdered was then distributed uniformly over the plate by rubbing down with the finger. In this way very thin and uniform films were obtained which contained approximately .4 mgr. a square cm. In all cases the uranium X was first separated by the "iron method" in order to avoid any effects due to soft or hard β rays. For the purpose of making a comparison under practically identical conditions of the ionization curves of uranium and ionium, a trace of highly concentrated ionium was mixed with about a hundred times the quantity of uranium oxide. The materials were dissolved in acid in order to secure their complete mixture; the solution was then evaporated to dryness and the residue changed into oxide. This material was then distributed on a glass plate in exactly the same way as described above for the pure uranium oxide. On account of the presence of the ionium, this uranium film was now about 30 times as active as an ordinary pure uranium film. Another uranium film containing a trace of polonium was also prepared in a similar way. In this case the activity of the film was about 28 times greater than that of a pure uranium film. This method of preparing the films ensured that the absorption, if any, in the matter itself would have affected the ionization curves in the three cases in exactly the same way.

Three typical curves are given in fig. 2, the ionization being plotted against the range of the α particles. Corrections

Fig. 2.



were made for the natural leak and also for the effect due to the uranium in the case of the ionium and polonium films. All three curves are typical of the ionization curve due to a parallel pencil of α particles in hydrogen. But while the curves for ionium and polonium completely agree with each other, the curve for uranium is distinctly different. In the latter case the maximum is not so sharply defined and the curve shows a much slower fall from the maximum towards the end of the range. To make this clear, the curve for ionium (see dotted line) is superposed on that of uranium, the ends of the two curves being made to coincide. The same difference between the curves was also brought out when the ionization was measured in hydrogen at a higher pressure or in air, or when slightly thicker films were used. As has already been pointed out, this cannot be due to the thickness of the film or to any other experimental cause.

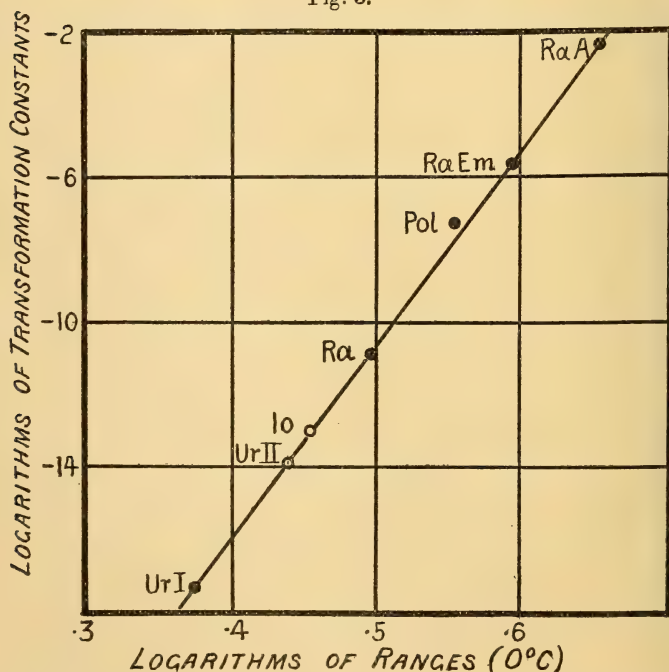
It seems, therefore, necessary to conclude that there exist two α -ray products in uranium which possess a slight difference of range. A determination of the difference of range of the two products could be made by comparison with a theoretical curve obtained by adding together two simple ionization curves of known difference of range. In this way it was found that by compounding two ionium or two polonium curves which were shifted relative to each other by 4 mm.,

a curve was obtained which agreed completely with the experimental curve for uranium.

Uranium consists, therefore, of two α -ray products whose ranges are 2.9 and 2.5 cm. in air at atmospheric pressure and at a temperature of 15°C . The value of the range of the α particles from uranium obtained by other observers and also previously by us (2.72 cm.), was obviously an average value of the two figures given above. No evidence has been obtained in these experiments of α particles of range 1.6 cm. as suggested recently by Friedmann*.

The above figure for the range of uranium, viz. 2.5 cm., is in much better agreement with the straight-line relation mentioned above between transformation constant and range, and fixes the straight line with a much higher degree of accuracy (see fig. 3). This is of special interest, since it

Fig. 3.



enables us to calculate the period of ionium and of the second product in uranium (uranium II.) with greater certainty than has hitherto been possible.

* F. Friedmann, *Wien. Ber.* cxx. p. 1361 (1911).

Uranium I. therefore, which has a period of 5×10^9 years, emits α particles of range 2.5 cm. in air at atmospheric pressure and at 15°C. , and is followed by another α -ray product, *uranium II.*, which has a period of about 2×10^6 years and emits α particles of range 2.9 cm. It is thus clear that in purified uranium preparations two successive α -ray products are present, differing in atomic weight by 4 units. These products must be very closely allied in chemical properties, for the experiments of many observers, amongst whom may be mentioned Boltwood and Soddy, have shown that it is impossible to reduce the α -ray activity of uranium by any chemical methods. A similar striking chemical affinity has been observed in the two elements thorium and ionium and also in a few other cases. Since the ratio of the two transformation constants of the two products in uranium is of the order of 10^3 , the amount of uranium II. in a gram of uranium is about one milligram. The presence of this small quantity of uranium II., differing only by 4 units from the atomic weight of uranium (238.5), can only affect a determination of the latter in the third decimal place.

Taking the range of the α particles from ionium as 3.00 cm. at 15°C. ($=2.84$ cm. at 0°C.), we find by interpolation from fig. 3 that it has a period of about 200,000 years, instead of the million years previously deduced.

Using the figures given in our previous paper, Swinne* has recently shown that the relation between range and transformation constant can be expressed in another form, but we postpone any discussion of this until the experiments on the ranges of the α particles from the products in the thorium series which are now in progress have been completed.

We wish to express our thanks to Prof. Rutherford for his kind interest and help in these experiments.

The Victoria University, Manchester,
Physical Laboratories.

XLI. Notices respecting New Books.

A Course of Plane Geometry for Advanced Students. Part II.
By CLEMENT V. DURELL, M.A. Macmillan & Co.: London, 1910.

IN the first part of this important work Mr. Durell dealt with the geometry of the straight line and circle. He now continues his method of treatment to the geometry of the conic. The nature of the treatment cannot be better described than in the following

* R. Swinne, *Phys. Zeitschr.* xiii. p. 14 (1912).

sentences from the Prefaces. "... a projective treatment introduces the student to a region of geometrical thought, unlike anything he has seen in the past—a transition as abrupt and fertile as the crossing from algebra to the calculus. There are constant surprises, apparent contradictions, features of absorbing interest, and principles which, by the generality of their application and the variety of their expression, cannot fail to fascinate the reader. . . . The theory of ideal elements in pure geometry, the notion of one-to-one correspondence and its application to homography and involution, the principles of conical projection are undoubtedly illuminated by a joint use of geometry and analysis." Chapters are devoted to such questions as orthogonal projection, conical projection, general projection, reciprocation, homographic ranges, involution ranges, etc.; and in almost every case each chapter is preceded by a short historic note tracing the origin and development of the idea or method. In many cases the proofs of important theorems are merely indicated and must be supplied by the student, and in addition there are numerous examples for exercise.

Homogeneous Coordinates for use in Colleges and Schools. By W. P. MILNE, M.A., D.Sc. Edward Arnold: London, 1910.

DR. MILNE has placed in the hands of the student a very serviceable exposition of the method of homogeneous coordinates, particular attention being paid to Areal and Trilinear. The five chapters treat respectively of the Straight Line, the Conic, Tangential Coordinates, the Circular Points at Infinity, and Parametric Representation. The discussion is simple and clear, and numerous examples are appended to the chapters for the student to test and strengthen his powers. In the preface Dr. Milne refers to certain methods in which "much memory work is avoided." Yet on page 71 he gives an "easy rule" in which an unnecessary appeal to memory is given for writing down the minors of a symmetrical determinant of the third order. The following is surely more satisfactory. Knowing the rule that a determinant of the third order is unchanged by cyclical permutation of rows or columns we get the minor with its proper sign by simply passing diagonally from left to right downwards to obtain the positive product in the minor. Could anything be simpler?

The Propagation of Electric Currents in Telephone and Telegraph Conductors. By Professor J. A. FLEMING, M.A., D.Sc., F.R.S. Pp. xiv + 316. London: Constable & Co. Ltd., 1911. Price 8s. 6d. net.

THIS book is an amplification of the notes of two courses of post-graduate lectures given by the author in the Pender Electrical Laboratory, University College, London, in 1910 and 1911. A considerable part of the subject matter has not hitherto found its way into textbooks. Professor Fleming has therefore rendered

a special service to this branch of electrical science in collecting the material for this textbook. Needless to say it is well done. It begins with a mathematical introduction which gives in a simple way the properties of vectors and their functions, leading up to the hyperbolic functions so successfully introduced by Professor A. E. Kennelley into the subject of alternating currents. Indeed, the book might almost be considered on its more theoretic side an exposition of Professor Kennelley's methods, so thoroughly is it saturated with them. These methods reduce to comparative simplicity the pioneer but elaborate investigations of Oliver Heaviside and Pupin on telegraphic and telephonic transmission.

The book is not, however, a merely abstract mathematical exposition. After the introduction it gives a thorough treatment of the many practical problems which have arisen, each one worked out numerically with reference to actual cables. The student is thus provided with a safe grounding by which he will be enabled to understand existing practice in such an intelligent way that he may well hope to advance beyond it by performing pioneer work himself.

Dr. Fleming is always happy in his exposition. Where difficulties and intricate points exist he is ready with an apt illustration. Numerous examples of this might be quoted from the present volume.

The book is excellently edited; we can find only a few trifling misprints. We are astonished, however, to find *distortion* spelt uniformly with *s* instead of the second *t*. Surely this is not in accordance with common practice. It is not English; nor was the change introduced when the word was made a technical word by Heaviside.

Bulletin of the Bureau of Standards. Vol. 7, No. 3. Washington: Government Printing Office, 1911.

THIS part contains some quantitative experiments in Long-distance Radiotelegraphy by L. W. Austin, being an account of experiments made by the American Navy Department between the scout-cruisers 'Birmingham' and 'Salem' and the large Fessenden station at Brant Rock. From these experiments the following equation is deduced for over-sea transmission:—

$$I_R = 4.25 \frac{I_S h_1 h_2}{\lambda d} \exp. \left(- \frac{.0015 d}{\sqrt{\lambda}} \right),$$

where I_R and I_S are received and sending currents, h_1 h_2 are antenna heights, λ is the wave-length, and d the distance apart, all lengths being given in kilometres. Messrs. E. Buckingham and J. H. Dallinger describe an extension of Paschen's method of equal ordinates to the computation of the constant C_2 of Planck's equation of radiation. It is shown that with sufficient accuracy

$$C_2 = 5\theta \frac{\lambda_1 \lambda_2}{\lambda_2 - \lambda_1} \left[(\log \lambda_2 - \log \lambda_1) - \frac{1}{5} \left(e^{-\frac{C_2}{\lambda_2 \theta}} - e^{-\frac{C_2}{\lambda_1 \theta}} \right) \right].$$

This differs from the value derived from Wien's formula by the exponential terms. It is also shown that

$$C_2 = 4.965 \lambda_m \theta, \text{ approximately,}$$

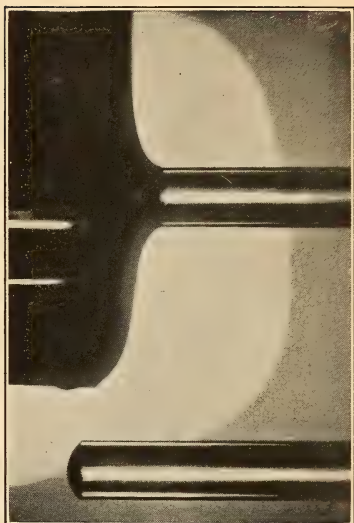
where λ_m is the wave-length for the maximum value of the radiation function at the temperature θ .

In a study of the current transformer with particular reference to iron bars by P. G. Agnew, the question of the meaning of Steinmetz' index is discussed. The number obtained by taking the slope of the logarithmic curve is not the index when the index is variable. This slope is, however, the more important datum in practice, and instead of existing names (such as logarithmic derivative) it is proposed to call it the ratio of variation. We confess that we think that no name could be chosen more successfully to hide the meaning of the quantity than this. The term logarithmic ratio would be more explicit and could be shortened in actual speaking in the well-known way. A very plausible way of calculating the index is given based on the employment of a point (as standard) at which the "ratio of variation" passes through either a maximum or a minimum. Values of this index are given for various flux densities for transformers of ordinary and silicon steel for frequencies of 30 and 60. They range from 1.36 to 1.71 for silicon steel, and from 1.49 to 1.71 for ordinary steel. But the method of calculation is in reality based upon an erroneous mathematical deduction on p. 449. The equation $d^2(\log y)/d(\log x)^2 = 0$ cannot be integrated because it applies only at one point of the curve. Nor is the ratio of variation equal to the exponent when the former is a maximum or a minimum. The truth is that any constant value of the factor K may be assumed and will yield correct values of the exponent if inserted in the equation $y = Kx^n$. The present writer, taking the same data for the transformer of ordinary steel, finds exponents which range from 1.73 to 1.81; and between flux-densities 100 and 16000 the greatest variation in the exponent is only 2.2 per cent. The value taken for $-\log K$ was 6.888.

Prof. H. S. Carhart discusses the thermodynamics of concentration cells. In the course of this discussion he criticises Nernst's third law of thermodynamics inasmuch as Nernst's assumption is at variance with the behaviour of concentration cells in which the free energy is proportional to the absolute temperature for very dilute solutions, or is equal to a constant plus a term proportional to the absolute temperature in other cases. Nernst's assumption makes the coefficient of the first power of the absolute temperature equal to zero. Numerous data are given showing that the e.m.f. of such cells is a linear function of the temperature.

The number also contains papers on the behaviour of high-boiling mineral oils on heating in the air, on the determination of vanadium in vanadium and chrome-vanadium steels, and on a comparison of American direct-current switchboard voltmeters and ammeters.

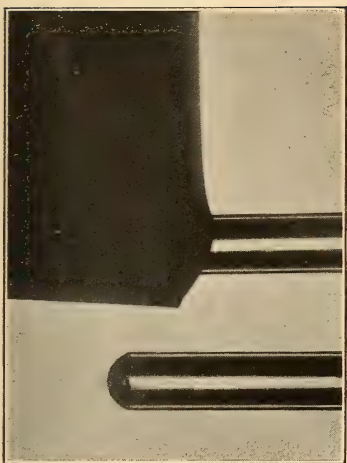
Fig. 6.



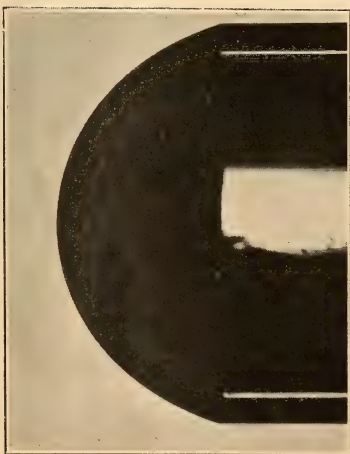
A.



B.



C.



D.

INDEX

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

APRIL 1912.

XLII. *Ionization by Moving Electrified Particles.*
By Sir J. J. THOMSON*.

THE theory developed in this paper is based on the following assumptions:—

1. Cathode or positive rays when they pass through an atom repel or attract the corpuscles in it and thereby give to them kinetic energy.
2. When the energy imparted to a corpuscle is greater than a certain definite value—the value required to ionize the atom—a corpuscle escapes from the atom, and a free corpuscle and positively charged atom are produced.

We must first find under what circumstances a cathode ray moving with a given velocity will lose when it passes by a corpuscle a quantity of energy greater than the amount required to ionize an atom.

In my ‘Conduction of Electricity through Gases’ it is shown that when a body with a charge E_1 in electrostatic units and mass M_1 is projected with a velocity V towards a body with a charge E_2 and mass M_2 at rest, the energy Q transferred to the latter is given by the equation

$$Q = \frac{4M_1M_2}{(M_1 + M_2)^2} T \sin^2 \theta,$$

* Communicated by the Author.

where T is the kinetic energy of the first particle, and

$$\sin^2 \theta = \frac{1}{1 + \frac{d^2 V^4}{e^2 E^2} \left(\frac{M_1 M_2}{M_1 + M_2} \right)^2},$$

where d is the length of the perpendicular from the second particle on the direction of projection of the first.

In the case of an encounter between a cathode ray and a corpuscle, $M_1 = M_2$ and $e = E$, and the equation becomes

$$Q = T \sin^2 \theta, \quad \sin^2 \theta = \frac{1}{1 + \frac{d^2}{e^4} T^2}.$$

In this case θ is the angle through which the cathode ray is deflected. Thus

$$Q = \frac{T}{1 + \frac{d^2}{e^4} T^2}, \quad \text{or} \quad d^2 = \left(\frac{T}{Q} - 1 \right) \frac{e^4}{T^2}. \quad (1)$$

Thus if the corpuscle requires an amount of energy W to escape from the atom, then, in order that the atom should be ionized by the cathode particle, d must not be greater than the value given by (1) when W is written for Q .

If n is the number of corpuscles in the atoms in unit-volume of the gas, the number of collisions for which d is not greater than the value given by equation (1) made per cm. by a corpuscle moving through the gas is $n\pi d^2$ or

$$\frac{n\pi e^4 \left(\frac{T}{W} - 1 \right)}{T^2};$$

this is a maximum when $T = 2W$.

When, as in the case of β rays or cathode particles in a vacuum-tube, T is large compared with W , the preceding expression reduces to

$$\frac{n\pi e^4}{WT},$$

so that the number of ions produced per cm. by a cathode particle on this theory varies as $1/T$.

Mr. Glasson (Phil. Mag. Oct. 1911) has shown that the number of ions made per centimetre by a cathode ray varies approximately inversely as the kinetic energy of the moving particle, so that his results are in accordance with this theory, in which it is to be remarked we have neglected the secondary ionization produced by the corpuscles expelled with

energy greater than W from the atom by the primary rays. The photographs taken by Mr. C. T. R. Wilson of the drops of water deposited on the ions produced by cathode rays show that this secondary ionization is not considerable.

For cathode rays with a velocity of 4.7×10^9 cm./sec. Glasson found that 1.5 pairs of ions were made per cm. of path in air at the pressure of 1 mm. of mercury, so that at atmospheric pressure 1140 pairs of ions would be produced per cm.

To compare this with the value given by our formula we require to know the value of W , the energy required to ionize an atom of the gas through which the ray is passing. This is a quantity to which very different values have been assigned by different observers, ranging in the case of air from that due to a fall of the atomic charge through 2 volts, found by H. A. Wilson, to that due to a fall through 175, the value given by Rutherford. The production of secondary positive rays by uncharged hydrogen molecules moving with a velocity not greater than 1.4×10^8 cm./sec. past corpuscles at rest, shows that the energy required to ionize an atom of hydrogen must be less than that possessed by a corpuscle moving at a speed of 1.4×10^8 cm./sec., which is equivalent to a fall through 5 volts. We shall take as the basis of our calculations for air Townsend's estimate of 10 volts.

Glasson's rays moving with a velocity of 4.7×10^9 cm./sec. had kinetic energy equivalent to a fall through 6000 volts:

$$\text{hence if } T = \frac{6000}{300} e, \quad W = \frac{10}{300} e, \text{ and } e = 4.7 \times 10^{-10},$$

$$n\pi e^4 = 1140 \times WT,$$

if n is the number of corpuscles per c.c. of air at atmospheric pressure. This gives $n = 10.7 \times 10^{20}$, the number of molecules in the air $= 2.7 \times 10^{19}$. Hence on an average there are about 40 corpuscles to the molecule. If the number of corpuscles in the atom were equal to the atomic weight, this number would have been about 30: hence, unless the value of W is very far out, we may conclude that the number of corpuscles in an atom is not greater than 2 or 3 times the atomic weight.

We shall proceed to the consideration of ionization by the β particles from radium. Eve (Phil. Mag. Oct. 1911) found that the β rays from radium produced 48 ions per cm. of path in air at atmospheric pressure; the velocity of these rays is not given, but we can test the formula by calculating from it what the velocity of the rays should be. Since Glasson's rays give 1140 ions per cm., and Eve's only 48,

the velocity of Eve's rays will be $\sqrt{1140/48}$, or 4.7 times those of Glasson's. As the latter rays had a velocity of 4.7×10^9 , the velocity of Eve's rays would be 2.2×10^{10} , which is a very reasonable value for the velocity of the β rays. We have neglected the correction for the alteration of the mass of the β rays with their velocity; this correction would have the effect of reducing slightly the calculated velocity of the β rays. As the ionization in a gas is equal to $\frac{ne^4}{WT}$, and

as n is proportional to the atomic weight of the gas, the number of ions produced by a cathode ray of given velocity moving through given gases will be proportional to the density of the gas divided by W , the energy required to ionize an atom of the gas. Hence W will vary as the density of the gas divided by the ionization per cm. of path. Kleeman (Proc. Royal Soc. lxxix. p. 220) gives the relative ionization in different gases produced by β rays. From his values I have calculated the relative values of Q for several gases:—

Gas ..	H.	C.	N.	O.	S.	Cl.	Br.	I.
W ...	1,	4.75,	5.26,	4.9,	3.6,	4.5,	5.4,	5.6.

Thus it would appear from this result that hydrogen is much more easily ionized than any of the other substances tried.

The deflexion which we have been considering of a rapidly moving corpuscle by another corpuscle would not give rise to much dissipation of energy by radiation. For the acceleration of one corpuscle is equal and opposite to that of the other; hence the electric force in one pulse will be equal and opposite to that in the other, so that when the pulse due to one overlaps that due to the other the energy will be small. The study of the positive rays in a discharge-tube shows, however, that sometimes a rapidly moving corpuscle is stopped and remains firmly attached to the atom when it collides with it. In collisions of this kind the energy of the corpuscle will be radiated away, and they may be regarded as the chief source of the Röntgen rays produced when cathode particles fall upon matter. That collisions of this kind occur is shown by the fact that atoms travelling with great velocity through a perforated cathode, and uncharged when they pass through the cathode, on passing through ionized gas at rest sometimes attract a corpuscle and become negatively charged. The conditions are the same as if the atoms were at rest, and the corpuscle moving with the velocity of the atom and colliding against it, the impact resulting in the stoppage of the corpuscle and its imprisonment by the atom.

Ionization by Positively Charged Particles.

In this case, as the mass of the moving particle is very large compared with that of the corpuscle, M_1 is large compared with M_2 , so that the equations

$$Q = \frac{4M_1M_2}{(M_1 + M_2)^2} T \sin^2 \theta, \quad \sin^2 \theta = \frac{1}{1 + \frac{V^4 d^2}{E^2 e^2} \left(\frac{M_1 M_2}{M_1 + M_2} \right)^2}$$

reduce to

$$Q = \frac{4TM_2}{M_1} \sin^2 \theta, \quad \sin^2 \theta = \frac{1}{1 + \frac{d^2 M_2^2 V^4}{E^2 e^2}};$$

or if T' is the kinetic energy of a corpuscle moving with the velocity of the positive particle,

$$Q = 4T' \sin^2 \theta; \quad \sin^2 \theta = \frac{1}{1 + \frac{4T_1^2 d^2}{E^2 e^2}},$$

or

$$d^2 = \left(\frac{4T'}{Q} - 1 \right) \frac{e^2 E^2}{T'^2}.$$

Thus the number of ions made per centimetre of path by the action of the positively charged particles on the negative corpuscles is, when T' is large compared with W ,

$$\frac{n\pi e^2 E^2}{WT'}.$$

Thus when $e=E$ the number of ions produced by the positively electrified particle is the same as the number produced by a corpuscle moving with the same velocity. When, as in the case of the α particles, $E=2e$, the ionization produced by the α particle is four times that produced by a corpuscle moving with the same velocity. We can test this result by comparing the ionization due to the α particles from radium C, which have an initial velocity of 2.06×10^9 cm./sec., with that due to Glasson's cathode rays with the velocity of 4.7×10^9 cm./sec. In consequence of the slower velocity the α particles ought by our rule to make $(4.7/2.06)^2$ or 5.4 times the number made by the cathode particles, and in consequence of the double charge 4 times the number; hence the α particle should make 4×5.4 or 21 times as many as the cathode ray. As the cathode ray makes 1140 the α particle should make 23940 ions per centimetre; the number as measured by Geiger is 22500, the difference is not greater than could be accounted for by errors in the experiments.

In order that a positively charged particle may ionize a gas at all T' must be greater than $W/4$; thus if we take W to be represented by 10 volts, T' must be at least 2.5 volts. Thus T , if the positively charged particle were an atom of hydrogen, must be 2.5×1700 or 4250 volts; if it were a molecule of hydrogen it would be 8500 volts, if an atom of oxygen 68000 volts. Thus in the case of the positive rays produced in a vacuum-tube, unless the potential difference between the terminals is very large, it will only be the atoms and molecules of the lighter gas which can produce ionization in the way we are considering.

According to this view it is the velocity of the positive particle and not its energy which must exceed a critical value before it can ionize a gas, and a knowledge of this critical value would enable us to find the value of W . It would I think be easier to determine W by experiments on positive particles than with negative ones; and I hope by isolating by means of magnetic and electric deflexions positive rays of definite character and velocity, to get information on this point.

In the preceding investigations we have supposed that the corpuscles in the atom were free; the amount of energy communicated to a free corpuscle will not, however, differ appreciably from that given to one held bound by the forces exerted on it by its neighbour, if the time of oscillation of the corpuscle under these forces is large in comparison with the time during which the forces due to the moving particle are appreciable. This time will be of the order d/V , and when the particles are moving with a velocity of 10^9 cm./sec. this time will be of the order 10^{-18} sec., which is very small in comparison with the time of any vibrations revealed by the spectroscope. For very slow cathode rays or positively charged particles, the influence of the forces inside the atom might be appreciable and reduce the energy communicated to the corpuscle. These forces will in any case naturally deflect the corpuscle on its way out of the atom, and make it emerge in a different direction from that in which it started after its encounter with the moving particle. We can easily show that this direction makes an angle $\pi/2 - \theta$ with the original direction of motion of the particle, so that when θ is small this direction is at right angles to the direction of the primary rays.

Radiation produced by the Recombination of Ions.

When a corpuscle is liberated from an atom or molecule, a definite amount of work W is required, which is equal to

the potential energy of the positively charged residue and a corpuscle at an infinite distance from it. If the work spent on the corpuscle is greater than W , the corpuscle leaves the atom with a finite amount of kinetic energy, but the state of the positively charged ion and its potential energy with respect to a distant corpuscle is not affected. Consider now what happens when this positive ion and a corpuscle combine and restore the atom or molecule to the state in which it existed before ionization took place. Under their mutual attraction the corpuscle and positively charged ion approach each other and acquire kinetic energy. As the mass of the corpuscle is much the smaller, the kinetic energy will be almost entirely localized in the corpuscle. After the corpuscle has fallen back into the ion it will have an amount of kinetic energy equal to W , if there has been no dissipation of energy by radiation; before the atom is restored to the state it was in before ionization, this energy must be got rid of. This dispersal of the energy is accomplished by its radiation, which takes place as long as its motion is being accelerated. Thus from the time of commencement of the recombination up to that when the atom has become normal, a stream of radiation is emitted from the system, constituting a pulse, which may be a linear one, of electromagnetic radiation, whose duration and energy depend only on the properties of the atom or molecule. Hence the character of the radiation emitted during the recombination of the ions will be a series of pulses, each pulse containing the same amount of energy, and of such a character that if we were to analyse the electromagnetic disturbance by Fourier's theorem into a system of harmonic vibrations, the distribution of energy among the different periods would be the same for each pulse. In fact, each of these pulses will form a unit or quantum, and the total radiation will be built up of such units.

Now, what will be the nature of this radiation? If we resolve it up into light-vibrations, where will the maximum energy be? will it be far down in the infra-red or high up in the ultra-violet? This will depend on the energy required to ionize a molecule. To fix our ideas let us suppose this is represented by 10 volts, so that when the corpuscle regains the atom or molecule it will be moving with the velocity corresponding to the fall of the atomic charge through 10 volts. We may fairly compare the radiation it emits with that emitted by a corpuscle moving with this velocity when it strikes against a molecule. If we suppose that the radiation from hot bodies is due to the electric waves generated when corpuscles in thermal equilibrium with the body

strike against the molecules of the body, the character of the radiation emitted when the ions recombine will be comparable with that from a body at such a temperature that the average energy of one of its molecules is that due to the fall of the atomic charge through 10 volts. At the temperature 0°C . the average energy of a molecule of a gas is that due to the fall of the atomic charge through $1/30$ of a volt, which is $1/300$ part of the energy of our corpuscles; the absolute temperature of a body whose molecules have energy equal to the corpuscle is thus 300×273 , or about 80,000 degrees absolute: this is about 13 times the absolute temperature of the sun, and as the maximum energy in the solar spectrum is in the neighbourhood of wave-length $4.9 \times 10^{-5}\text{ cm.}$, and as the wave-length for maximum energy is inversely proportional to the absolute temperature, the maximum energy for light analogous in its properties to the radiation emitted by the recombination of the ions would be in the neighbourhood of wave-length $3.8 \times 10^{-6}\text{ cm.}$, and would thus correspond to light very far in the ultra-violet. The theory is supported by the fact that those regions in a discharge-tube where recombination is taking place, such as the negative glow, are the sources of a type of radiation called "Entladungstrahlen" which has many of the properties of ultra-violet light.

Suppose now that besides the corpuscles which can be dislodged from the atom by the expenditure of an amount of energy measured by a few volts, there are in the atom other systems which require for their dissociation a much greater amount of energy, say an amount measured by thousands of volts. If the ionization of these systems is to be effected by cathode rays, it will not begin unless the rays have the velocity due to this number of volts; when, however, the rays have a greater velocity than this, some of these systems will be ionized, and a positive residue produced which will have with respect to a corpuscle at some distance away potential energy measured by x thousand volts. When the residue and the corpuscle unite and reproduce the original system, this amount of energy will have to be radiated away; and the type of the radiation will be such that it is represented by waves with wave-lengths less than those in the preceding case in the proportion of $1:100x$. Thus the maximum energy would be in the neighbourhood of wave-length 10^{-8} cm. , *i. e.* the radiation would be Röntgen radiation. Thus the presence in the atom of systems requiring a large quantity of energy to ionize them, would give rise to Röntgen radiation of a type determined solely by the properties of the atom. The energy in this radiation would be

divided into definite units or quanta, the character of the radiation when excited would be independent of the means used to excite it, but it would not be excited unless the velocity of the primary cathode rays exceeded a critical value.

This radiation has all the characteristics of the "characteristic Röntgen radiation" discovered by Barkla. Barkla made the very important discovery that any element whose atomic weight is greater than 39 gives out, when exposed to Röntgen radiation or cathode rays, secondary Röntgen radiation whose type depends only on the nature of the element. For the same element the "characteristic" radiation is the same whatever be the character of the primary radiation, with this proviso, that the characteristic radiation is not excited unless the primary Röntgen rays are "harder" than the characteristic radiation, or if the cause of excitation is cathode rays unless these are moving faster than a certain critical velocity; these are just the characteristics of the radiation emitted during the recombination of the systems of the kind we have been considering. Whiddington has shown that the least velocity of the cathode ray which can excite the characteristic radiation of an atom of atomic weight A is, in the case of all the elements he investigated, approximately equal to $10^8 A$ cm./sec.

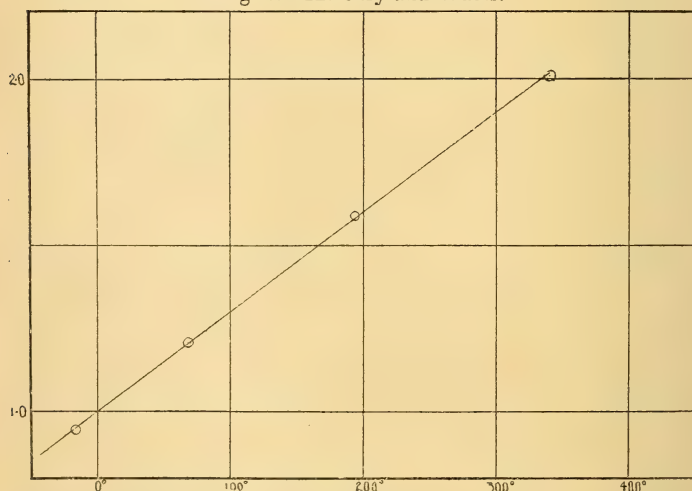
The existence of systems which are first dissociated and then restored to their original condition by the falling in of a corpuscle carrying with it kinetic energy, will also explain the diminution of specific heat with temperature. For if this is the way by which kinetic energy is communicated to the system, it is necessary that the system should first be dissociated. If this is to be done by corpuscles their energy must exceed a certain value w . The kinetic energy of the free or quasi free corpuscles in a body is proportional to the absolute temperature θ , let it equal $\alpha\theta$. Then when $\alpha\theta$ is $< w$ the system will not absorb energy and so will not affect the specific heat, but when $\alpha\theta$ is $> w$ the system can be dissociated, can therefore absorb energy and therefore increase the specific heat; the specific heat therefore will be greater when $\alpha\theta > w$ than when $\alpha\theta < w$. If we calculate on these lines the specific heat of a body whose molecules contain systems which require for their dissociation $w_1, w_2, \dots w_n$ units of work, and suppose that the energy is distributed among the corpuscles according to Maxwell's law, we get an expression for the specific heat as a function of temperature of the same form as that given by Einstein, which is in accordance with the remarkable results obtained by Professor Nernst and his pupils at very low temperatures.

XLIII. *Notes on the Viscosity of Liquids.* By ALFRED W. PORTER, F.R.S., *Fellow of and Assistant Professor of Physics in University College, London* *.

1. *The Variation of Viscosity with Temperature.*

WHEN two liquids are examined throughout a sufficient range there can, in general, be found a temperature for the second liquid at which its viscosity is the same as that for the first liquid at any given temperature. Let this temperature, when the standard liquid is at T_0 , be represented by T . Then if $\frac{T}{T_0}$ be plotted against T , I find that the curve obtained is practically a straight line. This statement is illustrated for the case of mercury with water chosen as the standard substance in fig. 1.

Fig. 1.—Mercury and Water.



The values obtained by interpolation from the data given by Landolt and Börnstein are as follows :—

Viscosity.	Water. T_0 .	Mercury. T .	$\frac{T}{T_0}$.
·0181	0° C.	— 16° C.	·942
·0133	10	+ 68	1·206
·0102	20	+194	1·593
·0090	25	+340	2·06

* Communicated by the Author.

These values practically cover the range for which coincident values exist for the two liquids; in fig. 1 $\frac{T}{T_0}$ is plotted against T , and a straight line is drawn so as to lie closest to the points.

This method of plotting is similar to that employed by Ramsay and Young in connecting together the vapour-pressures of different liquids.

On a former occasion (Phil. Mag. June 1907, p. 724) I showed that in so far as that curve may be taken as perfectly straight, it must be possible to represent the vapour-pressure of each of the substances concerned by the formula

$$f(p) = A + \frac{B}{T};$$

where $f(p)$ stands for a function of p which must be the same for both liquids, and A and B are constants characteristic of each liquid.

Applying the same reasoning to the present problem, we see that in so far as the curve such as fig. 1 may be taken as perfectly straight it must be possible to represent the viscosities (μ) or the mobilities ($M=1/\mu$) by the formula

$$F(M) = f(\mu) = A + \frac{B}{T}.$$

A formula of this type fits even such an extreme case as that of the viscosity of pitch as some, at present unpublished, results obtained by Mr. G. B. Jeffery show.

The case in which mercury and water are the two liquids compared is specially interesting, because water is a strongly associated liquid while mercury is considered to be non-associated. In the corresponding vapour-pressure problem it is usually concluded that a deviation from straightness indicates that one of the vapours "undergoes dissociation on heating" or "that there is molecular association in the liquid state" *. It would seem that the degree of curvature cannot be taken as a criterion of the degree of association in the analogous viscosity problem.

Similar curves have been obtained for bromine and water, oil of turpentine and water, ethyl ether and benzole, ethyl acetate and benzole, in each case with similar results.

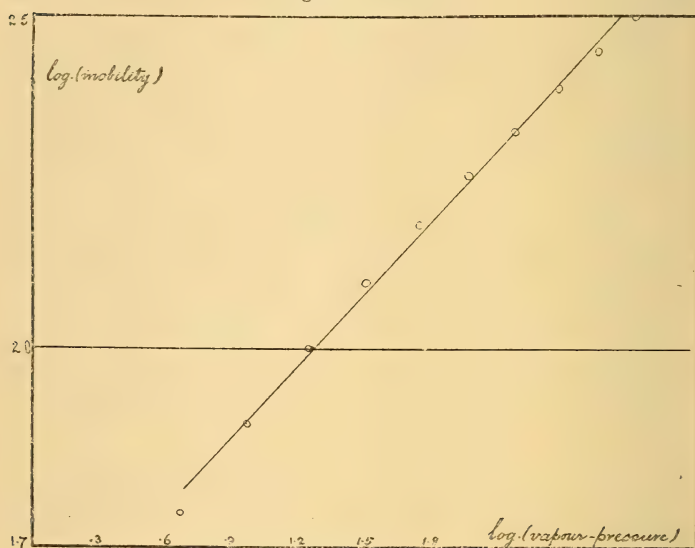
2. Mobility and Vapour-pressure.

The discovery of the above similarity between a problem in connexion with vapour-pressures and one in connexion with viscosities (or mobilities) suggested that other relations

* Young, 'Stoichiometry,' p. 145.

might be found between them. As a matter of fact, it is found that if the logarithm of the mobility be plotted against the logarithm of the vapour-pressure, a curve differing very little from a straight line is obtained both in the case of mercury and in that of water. These curves are shown in figs. 2 and 3.

Fig. 2.—Water.



The greatest deviation in the case of mercury only corresponds to less than 6 parts in 1000 in the value of the mobility. It is scarcely likely that the experimental values are correct to this degree of accuracy, although the smoothness of the *curve* which may be drawn amongst them would seem to indicate otherwise. It must be remembered that the corrections for kinetic head &c. which are usually applied in connexion with Poiseuille's method are of uncertain validity* and they may easily introduce a fictitious curvature.

The equation to the straight line for mercury (fig. 3) is

$$\log M = .0403 \log p + 1.938,$$

and for water (fig. 2) is

$$\log M = .362 \log p + 1.54.$$

* L. R. Wilberforce, *Phil. Mag.* 1891; Hagenbach, *Pogg. Ann.* cix.; Franz Neumann, *Leçons* (1858-59: published after his death); Couette, *Journal de Physique*, 1890, p. 414; Menneret, *Journal de Physique*, October 1911.

Fig. 3.—Mercury.

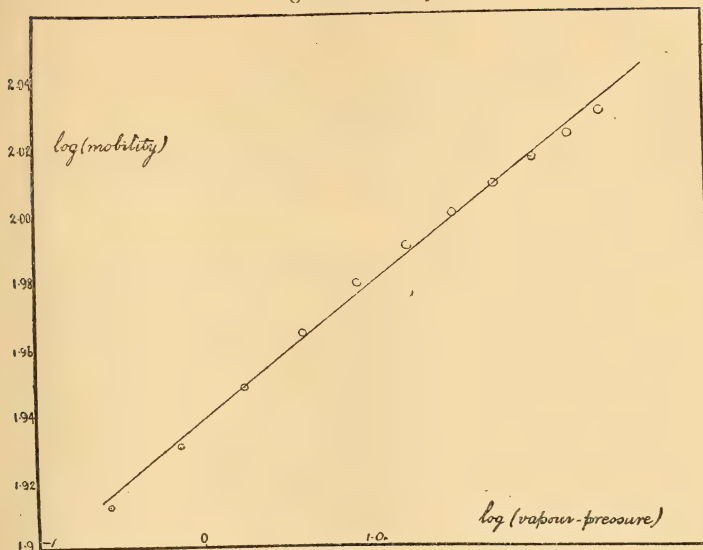
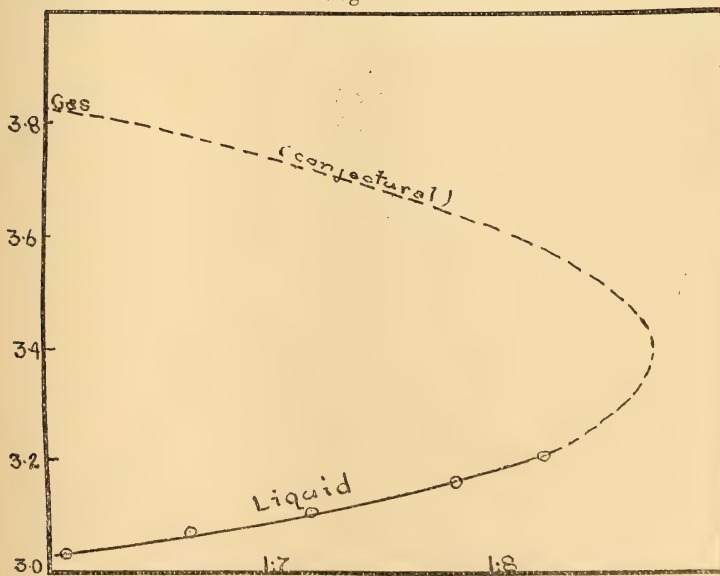


Fig. 4.



Log (mobility) against Log (vapour pressure).

Such published evidence as exists at present is, in fact, rather in favour of a curvature in the opposite sense. In fig. 4 are shown the values obtained by Warburg and Babo *

* Wied. Ann. xvii. (1882) pp. 390-427.

for carbon dioxide for various saturation pressures, together with the accepted value for the gas at ordinary pressures. It will be seen that the curve for the liquid is concave upwards. The values shown for the liquid and gas are connected together conjecturally by means of a dotted curve, on the assumption that the mobility varies continuously through the critical point. It is of some interest that the curve so obtained is very nearly indeed a parabola with its axis horizontal.

3. I am not aware that it has ever been pointed out that those liquids which have a small viscosity at ordinary temperatures have, in general, a great vapour-pressure. This law holds perfectly for homologous liquids, and it holds, so far as order of magnitude is concerned, in all other cases. It is needless to multiply instances: a glance at Landolt and Börnstein's Tables exhibits the law at once; but, as extreme cases, may be mentioned that of glass (which is a super-cooled liquid) with its very large viscosity and negligible vapour-pressure, and that of liquid CO_2 , which has larger vapour-pressure and a smaller viscosity than that of any other liquid on which measurements have been made.

XLIV. *Ionization by Alpha Rays.*

By NORMAN CAMPBELL, *Sc.D.**

1. **I**N two previous papers on "Delta Rays"† it was shown that it was extremely improbable that the delta rays had an initial velocity as great as that corresponding to the 20 volts which had previously been accepted. It was further shown that the speed of the rays, if it was greater than a small fraction of a volt, must be independent of the speed of the exciting rays, and nearly, if not quite, independent of the material from which they are emitted. These conclusions appeared of sufficient interest and importance in their bearing upon the general problem of the mechanism of radiation to make it worth while to attempt to establish them on a firmer basis by experiments of a different nature. The following pages contain an account of these experiments, which confirm all the conclusions put forward already, and produce, as a side issue, some results of a different nature. After the experimental evidence has been explained, the bearing of it on the main problem under discussion is considered.

* Communicated by the Author.

† Campbell, *Phil. Mag.* Aug. 1911, p. 276, and Jan. 1912, p. 46.

PART I.

Qualitative Measurements.

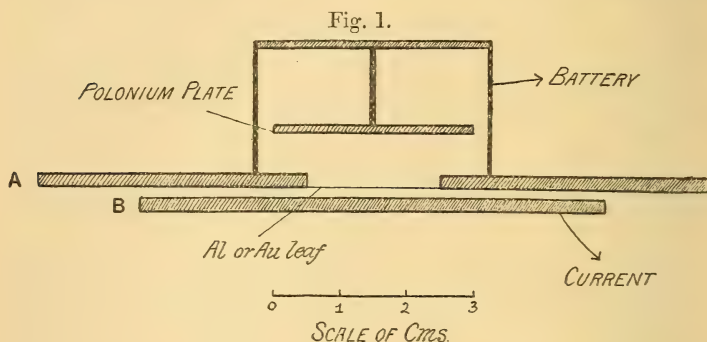
2. It was thought that additional information might be obtained as to the nature of the delta rays by experiments on ionization by collision. If the power of an ion to form new ions when it collides with neutral atoms depends on its velocity when it collides, two ions will have different powers in the same electric field if they start with different velocities.

Consider a layer of gas contained between parallel electrodes A and B, composed of different materials. α rays pass through A and the layer of the gas, being finally absorbed in B; they excite delta rays at both A and B, and produce ionization in the gas. An electric field is established between A and B of an intensity sufficient to cause ionization by collision; the former experiments in a vacuum have shown that it will also be sufficient to prevent any of the delta rays leaving the positive electrode, and to ensure that all the delta rays leave the negative. The current arriving at the electrodes due to the ionization in the gas must be the same for both directions of the electric field if the ionization in the gas is uniform; but if the delta rays emitted from A are different, either in quantity or in quality, from those emitted by B, the current due to the delta rays from the electrodes will differ according to the direction of the field. When A is positive this part of the ionization will be caused by the delta rays from B; when A is negative it will be caused by the delta rays from A.

If the delta rays differ in initial velocity the difference between the currents in the two directions should be almost independent of the intensity of the field, so long as it is sufficient to cause ionization by collision at all; for after the electrons, which are liberated as delta rays, have made a few collisions all trace of their original velocity will be lost; any difference in initial velocity will appear only in a difference in the fraction which ionize at their first collision. But if the rays differ in quantity, there will always be more ions in the gas in one case than in the other, and the difference between the currents in the two directions should increase steadily with the intensity of the field.

3. The electrodes of the apparatus in which the measurements were made are drawn to scale in fig. 1. A and B are

the parallel electrodes, B being connected to the apparatus for measuring the current, while A was connected to a source of potential. The α rays emitted by the polonium plate P



issued through the hole in A, covered with a thin foil of the material under investigation. The dimensions were arranged so that all α rays which passed through A and were not greatly scattered struck B.

The electrodes were contained in an air-tight chamber, and the pressure of the dry air in it measured by a McLeod gauge. Pressures throughout this paper are expressed in millimetres of mercury reduced to 15° C. The current was measured by the method involving the use of high resistances described in a former paper*.

4. The results of the measurements are given in Tables I.-IV. For Table I. A was covered with gold and B with aluminium; for Table II. the position of these materials was reversed; for Tables III. and IV. both A and B were covered with the same material, aluminium and gold respectively. The first row of figures gives the pressure of the air at which the experiments were made; the subsequent rows the values of the current for potential differences between A and B given in the first column. The columns marked "sum" contain the arithmetical sum (or algebraical difference) of the currents measured with the electric field in opposite directions; the columns marked "diff." give the arithmetical difference (or algebraical sum) of the same currents. The unit of current is about 2×10^{-12} ampere. The figures in different columns are not strictly comparable; allowance has to be made for the decay of the polonium and for slight alterations in its position when the apparatus

* Phil. Mag. Aug. 1911, p. 301.

was taken down. *In all cases the positive current (i. e. that with A positive) was greater than the negative ; so that the figures in the columns marked "diff." have always the same sign.*

5. It will be observed that the difference of the currents in the two directions is never zero. Such a result is to be expected, for the α rays give up their charge to B, and the current due to this cause is not reversed when the field is reversed. But part of the difference is due to Volta differences of potential in the measuring apparatus ; the magnitude of this part was quite constant over long periods of time, but was apt to change when alterations were made in the apparatus. Measurements of its magnitude were made, but they are unimportant for the present purpose.

It will be observed that in Tables III. and IV., when the electrodes are covered with the same material, the difference between the currents is almost or quite constant for all values of V. The difference may decrease slightly, which means that the delta rays from B produce slightly less ionization than those from A ; an effect of this nature may be attributed to an absorption of the α rays in passing between A and B. But it may be confidently concluded (1) that the apparatus is satisfactory in that all the rays which emerge from A strike B, and (2) that there is no difference to be detected between the "emergence" and "incidence" radiation of delta rays ; for the rays from A are "emergent," those from B "incident." Any difference in the two forms of radiation, which was indicated in the former experiments, must be attributed, as was suggested before, to the many sources of uncertainty to which the interpretation of the measurements was liable.

In Tables I. and II., however, the differences between the currents change markedly when the potential difference is increased. But this change cannot be attributed to a difference in the ionization caused by the delta rays from gold and aluminium, because it does not change its sign when the position of those materials is reversed. In Table II. the increase of the positive current relatively to the negative, if attributed to a difference in the delta rays from the two electrodes, would signify that more ionization is produced by the delta rays from aluminium ; in Table II. it would signify that more ionization is produced by the rays from gold. The current flowing from A to B always increases relatively to that flowing from B to A with whatever material the electrodes are covered. The effect could be attributed to some geometrical asymmetry, were it not apparently dependent on

TABLE I.—Gold above,

p	0.004		0.54		0.77		0.95	
	sum	diff.	sum	diff.	sum	diff.	sum	diff.
V=20.....	2.05	0.55	3.00	0.54	3.40	0.46	3.62	0.50
30.....	2.05	0.54	3.25	0.55	3.69	0.49	3.98	0.52
40.....	2.04	0.53	3.45	0.55	4.00	0.50	4.36	0.56
50.....	...		3.67	0.57	4.31	0.51	4.73	0.57
60.....	...		3.84	0.60	4.61	0.55	5.10	0.60
70.....	...		4.00	0.62	4.89	0.59	5.46	0.64
80.....	...		4.12	0.62	5.09	0.61	5.81	0.67

TABLE II.—Gold below,

p	0.036		0.27		0.63.		0.87	
	sum	diff.	sum	diff.	sum	diff.	sum	diff.
V=20.....	2.88	0.49	3.13	0.54	4.24	0.51	4.58	0.48
V=30.....	2.94	0.49	3.38	0.52	4.62	0.54	5.04	0.49
V=40.....	2.94	0.49	3.50	0.58	5.00	0.55	5.53	0.51
V=50.....	2.97	0.50	3.62	0.53	...		6.05	0.53
V=60.....	3.01	0.50	3.73	0.55	5.74	0.57	6.54	0.56
V=70.....	3.01	0.49	...		...		...	
V=80.....	3.02	0.49	3.88	0.56	6.32	0.58	7.48	0.66

TABLE III.—Aluminium above and below.

p	0.51		1.0		1.46		1.94		2.4	
	sum	diff.	sum	diff.	sum	diff.	sum	diff.	sum	diff.
V=20.....	2.78	0.22	3.50	0.26	4.13	0.19	4.82	0.26	5.44	0.26
V=30.....	2.98	0.22	3.83	0.25	4.53	0.17	5.25	0.27	5.84	0.24
V=40.....	3.16	0.22	4.18	0.24	4.99	0.19	5.74	0.26	6.36	0.24
V=50.....	3.31	0.23	4.55	0.25	5.50	0.20	6.38	0.28	7.03	0.23
V=60.....	3.46	0.24	4.92	0.24	6.03	0.19	7.09	0.27	7.83	0.23
V=70.....	3.57	0.23	5.26	0.24	6.60	0.18	7.83	0.23	8.76	0.24
V=80.....	3.69	0.23	5.57	0.25	7.20	0.20	8.67	0.23	9.78	0.22

Aluminium below.

1.20		1.55		1.98		2.15		2.29		2.60	
sum	diff.	sum	diff.	sum	diff.	sum	diff.	sum	diff.	sum	diff.
4.04	0.52	4.50	0.46	5.33	0.55	5.58	0.48	5.72	0.50	6.36	0.50
4.43	0.53	4.95	0.47	5.73	0.53	5.98	0.48	6.13	0.51	6.75	0.51
4.88	0.58	5.47	0.51	6.31	0.51	6.53	0.49	6.70	0.50	7.31	0.51
5.40	0.60	6.09	0.57	7.02	0.56	7.27	0.51	7.42	0.48	8.05	0.55
5.91	0.63	6.72	0.60	7.79	0.59	8.10	0.54	8.22	0.48	8.94	0.54
6.43	0.67	7.42	0.66	8.66	0.62	9.02	0.58	9.23	0.51	10.00	0.60
6.92	0.70	8.11	0.71	9.61	0.69	10.07	0.63	10.26	0.62	11.18	0.62

Aluminium above.

1.17		1.33		1.65		1.90		2.48	
sum	diff.	sum	diff.	sum	diff.	sum	diff.	sum	diff.
5.24	0.49	4.59	0.40	5.28	0.46	5.71	0.41	6.83	0.45
5.83	0.48	5.06	0.43	5.76	0.50	6.16	0.44	7.15	0.45
6.46	0.50	5.61	0.46	6.44	0.50	6.79	0.47	7.59	0.44
7.13	0.52	6.24	0.48	7.23	0.57	7.54	0.49	8.31	0.45
7.87	0.54	6.87	0.53	8.04	0.63	8.43	0.50	9.26	0.48
8.60	0.56	7.52	0.56	8.91	0.72	9.45	0.57	10.36	0.51
9.34	0.62	8.21	0.61	9.87	0.76	10.52	0.60	11.61	0.60

TABLE IV.—Gold above and below.

<i>p</i>	0.53		1.06		1.38		2.0		2.43	
	sum	diff.	sum	diff.	sum	diff.	sum	diff.	sum	diff.
V=20.....	2.50	0.26	3.30	0.30	4.19	0.45	5.05	0.45	5.74	0.44
V=30.....	2.72	0.24	3.71	0.25	4.61	0.45	5.51	0.45	6.21	0.43
V=40.....	2.70	0.24	4.08	0.24	5.08	0.44	6.04	0.46	6.74	0.44
V=50.....	3.07	0.23	4.46	0.24	5.59	0.43	6.67	0.43	7.42	0.42
V=60.....	3.22	0.22	4.82	0.22	6.12	0.44	7.42	0.42	8.22	0.38
V=70.....	3.33	0.21	5.18	0.20	6.65	0.45	8.20	0.46	9.15	0.41
V=80.....	3.43	0.19	5.51	0.21	7.21	0.43	9.04	0.44	10.19	0.39

the presence of two different electrodes. I have no explanation to offer of the effect, but it does not seem to prevent the conclusion that the delta rays from aluminium and from gold excited by the same alpha rays are the same both in quantity and in quality. Several other experiments of a similarly qualitative nature were made and, though some unexpected phenomena were found, none of the measurements threw the smallest doubt on that conclusion. At length it appeared desirable to investigate the matter quantitatively by the aid of the detailed theory of Townsend; for this purpose more accurate and more extensive measurements were required.

PART II.

Quantitative Measurements.

6. In the experiments of Townsend, the theory of which is examined in the previous paper (Phil. Mag. March 1912, p. 400), the distance between the electrodes and not the pressure of the gas was altered. It appeared more convenient here to change the pressure of the gas and not the distance between the electrodes. An algebraic transformation suffices to reduce the equations to a suitable form. Adopting the notation of the previous paper,

$$\text{let } n' = n_0 l, \mu = \beta_0 l, \alpha' = \alpha_0 l, \nu = N_0 l, \frac{V}{p} = y, \frac{V'}{y} = c.$$

Then (13) becomes

$$i/\epsilon = e^{\mu p} \left\{ n_1 + n' \left(\frac{1}{\alpha'} + c \right) \right\} e^{-\mu c} - \frac{n'}{\alpha'}; \quad . \quad . \quad (1)$$

$$(15) \text{ becomes } \mu = \alpha' e^{-\mu c}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$(16) \text{ becomes } \alpha' = \nu e^{-\nu c}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$(18) \text{ becomes } \log \mu + \mu c = \log \nu - \nu c. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

It will be seen that if i , n , n' , p are measured for a sufficient number of values of y , it will be possible to determine the constants ν and V' .

The Experiments.

7. The experiments were carried out in the apparatus already described. The gas used was air dried by P_2O_5 . The pressure was read by a McLeod gauge calibrated experimentally. The different ratios (15, 20, 40, 200, 1000) were compared among themselves, and their relative values

known to $\frac{1}{2}$ per cent.* The smallest ratio was compared with a barometer gauge, and the absolute values thus known to 1 per cent. Pressures from 1–3 mm. were read to $\cdot 0025$ mm., from 3–6 to $\cdot 012$ mm., from 6–20 to $\cdot 025$ mm. The values are given in millimetres of mercury reduced to 15° C.

The currents were measured by the high resistance method as before. Owing to the wide range which had to be measured two resistances in the ratio of $5\cdot 281:1$ were employed. Currents less than 2 units (1 unit = $2\cdot 4 \times 10^{-11}$ amp., to within 5 per cent.) were measured to $\cdot 0005$ unit; those greater to $\cdot 003$ unit.

Differences of potential were measured to $0\cdot 2$ volt by means of a Weston laboratory standard voltmeter, said by its makers to be accurate in absolute measure to 1 in 1000.

8. Two complete series of measurements were taken, one with the electrodes covered with gold, the other with aluminium. In each series 6 or 7 values of y were chosen; for each of these values the relation between i and p was determined over the widest possible range of p . This range was limited on the lower side by $V=30$, the lowest potential difference for which the experiments in a vacuum had shown the delta-ray current to be saturated; on the higher side by the values of V and p at which, according to the figures given by Townsend, ionization by the positive ions was likely to become noticeable. Since the potential could only be varied conveniently in steps of about 2 volts, readings were taken on each side of the value of V determined by the measured pressure and the selected value of y , and the correct value found by interpolation. In every case two measurements were taken, one with the field from A to B and one with the field in the reverse direction; the arithmetic sum of the two currents is represented by the value of i . The experiments described above had shown that by this procedure a true value for the current due to the ionization caused by the alpha rays would be obtained, and the necessity of a knowledge of that part of the current which is unaffected by the field eliminated.

9. n' is the total number of ions made per second in the gas by the delta rays at a pressure of 1 mm. In order to determine this quantity measurements had to be made at pressures very much higher than any of those used in the other experiments, for it was only at pressures greater than 100 mm. that a sufficient approach to a saturation current

* The numbers given are only approximate, and represent what the ratios were intended to be when the gauge was made. That the values of y given in the table are not whole numbers is due to the difference between intention and realization.

could be obtained. At lower pressures noticeable ionization by collisions began before saturation was attained. It was found, however, that within the range from 100 to 700 mm. the current was very accurately proportional to the pressure, so that the interpolation to lower pressures does not introduce much uncertainty. And yet the greatest uncertainty in the experiments is connected with n' , for the values obtained on different occasions varied by as much as 4 per cent. (Allowance was made, of course, for the decay of the polonium; the accepted value $\lambda = 139$ (days)⁻¹ agreed well with the observations.) This uncertainty is probably due to the method of measurement adopted. After the experiments were finished—rather late in the day—a more complete investigation into the properties of the high resistances was undertaken. The results will be published shortly. It was found that the temperature coefficient was higher than had been suspected, and that there were sources of error connected with the lower resistance (by means of which n' was measured) which did not affect the higher resistance (which had been investigated before). If this inquiry had been made earlier a greater accuracy could certainly have been attained, but nothing has been found to throw doubt on the results. Indeed, the results of the measurements themselves may be judged to be good evidence of the value of the method employed.

n_1 , the number of ions liberated at the electrode per second, or, in these experiments, the number of delta rays excited there, can be ascertained by measuring the saturation current at the lowest pressures attainable (< 0.001 mm.). In the earlier observations this quantity was measured several times during the process of finding the relation between i and y , and the values obtained on a single day sometimes varied as much as 2 per cent. Moreover, the currents at higher pressures varied with n_1 , leading to some irregularity in the results obtained. (Thus in Tables XV. and XVIII. it will be seen that the points do not lie accurately on a smooth curve.) The variation was traced to the presence of an air-film on the surface of the electrodes, which increased the emission of delta rays from them. If the pressure was kept below 0.5 mm. the air-film was gradually destroyed; during three days when the pressure was kept as low as possible continuously, n_1 fell by 14 per cent. (The same change was noticed in the first paper on delta rays, p. 298.) Later, therefore, the pressure was never reduced below 0.5 mm. during the course of a set of experiments, and under these conditions there was no irregularity in the curves. n_1 was

determined occasionally by taking observations immediately the pressure had been sufficiently reduced, and it is these measurements, corrected for the decay of the polonium, which are used for the comparison made below.

TABLE V.

TABLE VI.

TABLE VII.

TABLE VIII.

GOLD. Oct. 6.		GOLD. Oct. 2.		GOLD. Sept. 14.		GOLD. Oct. 4.	
$y=102.2, n'=0.0766$		$y=71.54, n'=0.0794$		$y=51.1, n'=0.0835$		$y=40.83, n'=0.0776$	
<i>p.</i>	<i>i.</i>	<i>p.</i>	<i>i.</i>	<i>p.</i>	<i>i.</i>	<i>p.</i>	<i>i.</i>
0.423	0.152	0.477	0.148	0.78	0.198	0.942	0.194
0.516	0.169	0.634	0.177	0.88	0.214	0.952	0.195
0.644	0.196	0.751	0.202	1.04	0.248	1.104	0.231
0.748	0.221	0.862	0.228	1.09	0.261	1.332	0.271
0.886	0.260	0.944	0.248	1.23	0.308	1.415	0.284
1.015	0.311	1.000	0.264	1.53	0.384	1.579	0.329
1.110	0.352	1.133	0.303	1.58	0.396	1.889	0.404
1.228	0.405	1.299	0.356	1.76	0.466	2.051	0.457
1.336	0.465	1.415	0.406	2.02	0.570	2.357	0.563
1.385	0.495	1.550	0.467	2.25	0.680	2.527	0.624
		1.673	0.523			2.830	0.770
		1.746	0.569			2.992	0.842
		1.770	0.584			3.220	1.050
		1.891	0.645			3.447	1.122

TABLE IX.

TABLE X.

TABLE XI.

GOLD. Sept. 20.		GOLD. Sept. 22.		GOLD. Sept. 15.	
$y=31.11, n'=0.0820.$		$y=20.74, n'=0.0807.$		$y=10.37, n'=0.0835.$	
<i>p.</i>	<i>i.</i>	<i>p.</i>	<i>i.</i>	<i>p.</i>	<i>i.</i>
0.95	0.190	2.36	0.342	6.22	0.698
1.41	0.271	3.29	0.495	7.15	0.814
1.87	0.361	3.73	0.585	7.77	0.879
2.15	0.410	4.49	0.754	8.42	0.942
2.34	0.468	5.17	0.945	9.17	1.058
2.51	0.497	5.86	1.150	9.45	1.114
2.83	0.605	5.93	1.198	10.52	1.240
3.33	0.775	6.56	1.412	11.03	1.304
3.78	0.966	6.80	1.494	11.82	1.454
3.81	0.963	6.87	1.542	12.85	1.577
4.25	1.174	7.25	1.692	14.25	1.795
4.30	1.223	7.82	1.948	15.91	2.121
4.78	1.514	8.38	2.269	16.50	2.196
5.42	1.936	8.85	2.564	17.28	2.384
				19.12	2.724
				20.00	2.862
				21.43	3.215

TABLE XII.

TABLE XIII.

TABLE XIV.

TABLE XV.

ALUMINIUM. Oct. 19.		ALUMINIUM. Oct. 19.		ALUMINIUM. Oct. 23.		ALUMINIUM. Oct. 9.	
$y=102.2, n'=0.0733$		$y=71.54, n'=0.0767$		$y=51.1, n'=0.0705$		$y=51.1, n'=0.0802$	
<i>p.</i>	<i>i.</i>	<i>p.</i>	<i>i.</i>	<i>p.</i>	<i>i.</i>	<i>p.</i>	<i>i.</i>
0.355	0.130	0.552	0.149	0.732	0.162	0.688	.164
0.482	0.151	0.577	0.155	0.828	0.180	0.812	.188
0.561	0.169	0.759	0.190	1.202	0.246	0.979	.223
0.730	0.209	0.922	0.222	1.291	0.269	1.100	.249
0.874	0.249	1.025	0.247	1.662	0.365	1.286	.289
0.932	0.267	1.052	0.254	1.754	0.395	1.460	.338
0.999	0.292	1.168	0.294	1.978	0.478	1.583	.373
1.036	0.305	1.262	0.321	2.132	0.533	1.769	.437
1.140	0.343	1.392	0.359	2.227	0.571	1.941	.504
1.170	0.354	1.496	0.401	2.430	0.691	2.065	.545
1.272	0.401	1.529	0.412	2.597	0.772	2.422	.735
		1.645	0.472			2.545	.788
		1.766	0.524				
		1.976	0.644				
		2.001	0.661				

TABLE XVI.

TABLE XVII.

TABLE XVIII.

TABLE XIX.

ALUMINIUM. Oct. 20.		ALUMINIUM. Oct. 23.		ALUMINIUM. Oct. 10.		ALUMINIUM. Oct. 21.	
$y=41.48, n'=0.0705$		$y=31.11, n'=0.0695$		$y=31.11, n'=0.0786$		$y=10.37, n'=0.0702$	
<i>p.</i>	<i>i.</i>	<i>p.</i>	<i>i.</i>	<i>p.</i>	<i>i.</i>	<i>p.</i>	<i>i.</i>
0.932	0.178	1.060	0.181	1.206	0.209	3.85	0.369
1.398	0.258	1.537	0.245	1.701	0.282	5.30	0.484
1.469	0.260	2.002	0.324	1.783	0.314	6.64	0.620
1.875	0.361	2.425	0.407	2.153	0.374	7.92	0.745
2.008	0.403	2.89	0.519	2.195	0.374	8.99	0.854
2.117	0.430	3.355	0.658	2.278	0.417	10.12	0.979
2.50	0.558	3.822	0.822	2.677	0.484	12.37	1.232
2.76	0.654	4.294	1.037	2.753	0.538	14.0	1.464
2.95	0.740	4.737	1.274	3.627	0.592	14.62	1.510
3.225	0.886	5.212	1.554	3.161	0.623	15.86	1.680
3.274	0.911			3.232	0.685	17.10	1.853
3.42	1.004			3.634	0.784	18.22	2.025
3.71	1.198			3.710	0.866	18.90	2.124
3.89	1.327			3.731	0.852	21.11	2.521
				4.128	0.992		
				4.203	1.084		
				4.616	1.304		
				4.684	1.346		
				5.113	1.632		
				5.163	1.634		

The values of both n' and n_1 are, like the other currents, the arithmetical sum of the values obtained with the field in opposite directions.

10. Since the interpretation of the experiments is complicated and perhaps open to doubt, the readings themselves are given completely in Tables V.-XIX. The figures given are those actually recorded in the note-book, the only correction introduced being the reduction of the pressures to 15°C. ; no correction is made for the decay of the polonium. For two values of y for aluminium, two complete series of measurements were taken on different dates to ascertain the consistency of the results.

11. An attempt was first made to interpret the experiments on the assumptions that Townsend's formula (equation (7) of the previous paper) was correct. Each of the sets of measurements given in one of the Tables V.-XIX. was treated as a set of equations of the form (equivalent to (7))

$$i/\epsilon = \left(n_1 + \frac{n'}{\alpha} \right) e^{\mu p} - \frac{n'}{\alpha}, \quad (5)$$

in which i, p, y, n' were known and μ and n_1 unknown. The values of the unknowns were found by least-square calculation. It was found that the value of n_1 calculated was always about 0.6 of that found experimentally. Various sources of error were considered and investigated without result, till at last the suggestion occurred that the theory might be in error. As the result of examination, the error pointed out in the previous paper was detected, and the revised calculation given there made. Since the revised formulæ are far more complicated than (5), the former method of calculation was deemed unsuitable and was rejected.

12. Though the measurements which have been recorded will provide a test of the accuracy of the theory of ionization by collision, our primary object is not to examine this theory, but to obtain information about the delta rays. The properties of these rays are represented in our equations by n_1 ; n_1 is measured, but it is undesirable to take it as one of the variables known. For, if it were so taken, and only ν and V' treated as unknowns, the values of which were to be determined, it would be uncertain whether the discrepancies between theory and experiment, which appear when the calculated values are substituted in the equations, are due to errors connected with n_1 or to errors connected with some other of the quantities involved. It is preferable to retain

n_1 as an unknown, to calculate its values, and subsequently to compare the calculated and the observed values. Accordingly, the following method of successive approximations was adopted, the first of the two theories of the previous paper as to the nature of the negative ion being chosen provisionally.

It will be seen that, according to (1), the relation between i and p given in any one of the tables should be of the form

$$i = P e^{\mu p} + R.$$

It was assumed that the relation was of this form, and the values of P , R , and μ calculated from the measurements in each of the tables. The presence of three unknowns made the probable errors of calculation large, and attention was only paid to the values of μ obtained. These values, calculated by this method for the various tables, are given in Table XX. It will be observed that, within the rather large limits of error, there is no systematic difference between the values of μ for gold and for aluminium. Accordingly, all the values of μ , both for gold and aluminium, were taken as giving a single set of equations, similar to (4), whence the values of ν and V' might be calculated. The figures so obtained are given at the foot of the table.

13. An approximate value of R can now be calculated for each of the tables from the values of ν and V' together with the determined value of n' . Taking this value as correct, each of the tables now gives a set of equations of the form

$$i - R = P e^{\mu p},$$

from which P and μ can be determined. The necessary calculations were carried out, and the results are given in Table XXI. The new values obtained for μ are satisfactorily in accord with those determined before, and it appeared that nothing would be gained by repeating the same process of approximation. The values of i calculated from these values of P and μ , together with the approximate value of R , agreed thoroughly with those determined experimentally. In a few cases the difference between the calculated and observed values was greater than the uncertainty in a single measurement of the current, but no systematic divergence of the values for any given table could be detected. It may be confidently concluded that the curve is very nearly of the form assumed, and that the value of R adopted is very nearly correct.

TABLE XX.

GOLD.	$y =$	102.2	71.54	51.10	41.48	40.88	31.11	20.74	10.37
	$\mu =$	1.156 $\pm$ 0.5	0.809 $\pm$ 0.2	0.686 $\pm$ 0.1	...	0.531 $\pm$ 0.2	0.364 $\pm$ 0.1	0.217 $\pm$ 0.03	0.0535 $\pm$ 0.014
	$\mu =$	1.031 $\pm$ 0.03	0.871 $\pm$ 0.1	0.597 $\pm$ 0.1 0.635 $\pm$ 0.2	0.524 $\pm$ 0.06	...	0.411 $\pm$ 0.06 0.442 $\pm$ 0.1	...	0.0424 $\pm$ 0.03
ALUMINIUM.									

$$V' = 21.0 \pm 0.35. \quad v = 1.81 \pm 0.035.$$

TABLE XXI.

GOLD.	$y =$	102.2	71.54	51.10	41.48	40.88	31.11	20.74	10.37
	$\mu =$...	1.033 $\pm$ 0.1	0.848 $\pm$ 0.04	0.650 $\pm$ 0.02	...	0.569 $\pm$ 0.03	0.406 $\pm$ 0.02	0.252 $\pm$ 0.04	0.0458 $\pm$ 0.002
	$P =$...	0.132 $\pm$ 0.02	0.145 $\pm$ 0.01	0.176 $\pm$ 0.01	...	0.174 $\pm$ 0.02	0.236 $\pm$ 0.02	0.308 $\pm$ 0.01	1.885 $\pm$ 0.06
ALUMINIUM.	$\mu =$...	0.976 $\pm$ 0.08	0.839 $\pm$ 0.03	0.681 $\pm$ 0.05 0.666 $\pm$ 0.04	0.558 $\pm$ 0.01	...	0.411 $\pm$ 0.03 0.409 $\pm$ 0.02	...	0.0436 $\pm$ 0.002
	$P =$...	0.130 $\pm$ 0.01	0.136 $\pm$ 0.01	0.149 $\pm$ 0.02 0.163 $\pm$ 0.01	0.162 $\pm$ 0.01	...	0.214 $\pm$ 0.03 0.201 $\pm$ 0.01	...	1.601 $\pm$ 0.04

14. From these new and more accurate values of μ , ν and V' are again calculated. The results obtained are given at the head of Table XXII., in which the values of μ calculated are compared with those deduced directly from the curves. The agreement is not unsatisfactory, though it is not quite so good as that of the experiments of Townsend, considered in the previous paper. It is possible that the values of μ for aluminium are consistently somewhat smaller than those for gold, but the discrepancy is not greater than can be accounted for by the errors in n' already mentioned.

TABLE XXII.

$$V' = 20.75 \pm 0.08.$$

$$\nu = 1.807 \pm .008.$$

γ .	μ .	μ calc. — μ Au.	μ calc. — μ Al.
102.2	1.019	— .016	+ .043
71.54	0.839	+ .009	— .000
51.10	0.663	— .003	— .021 } — .003 }
41.48	0.554	...	— .004
40.88	0.547	— .022	
31.11	0.411	+ .005	.000 } + .002 }
20.74	0.229	— .003	
10.37	0.0443	— .015	+ .007

In the last stage of the approximation R is recalculated from the new values of ν and V' , and for μ the calculated value from Table XXII. used; P is then calculated for each of the tables; the value obtained for P is given in Table XXIII.; it will be observed that it differs very slightly from the previous approximation of Table XXI. From these values of P , n_1 is found by means of the relation

$$P = \left\{ n_1 + n' \left(c + \frac{1}{\alpha'} \right) \right\} e^{-\mu c}.$$

The value is given under n (calc.); in the column marked n (corr.) these values are corrected for the decay of the polonium, and all reduced to the same date; if the theory and the experiments were perfectly accurate the figures in this column would be constant. Since all the error in P is thrown on n_1 , in taking the mean the weights of the various values of n_1 are taking as inversely proportional to P , and the numbers in the column marked "error" are the divergences from the mean expressed as fractions of P . It will

TABLE XXIII.

y .	ALUMINIUM.				GOLD.			
	P.	n_1 (calc.).	n_1 (corr.).	Error.	P.	n_1 (calc.).	n_1 (corr.).	Error.
102.1	·1265	·0822	·0863	-2.3%	·1338	·0878	·0975	-2.8%
71.54 ...	·1361	·0799	·0839	-3.9	·1475	·0909	·0990	-1.6
51.1 ... {	·1504	·0870	·0930	+2.5	·1748	·0956	·0956	-3.3
	·1638	·0896	·0896	+0.2				
41.48 ...	·1645	·0851	·0900	+0.5				
40.88 ...	...	...	...	...	·1849	·0970	·1064	+2.8
31.11 {	·2161	·0867	·0930	+1.8	·2273	·0929	·0960	-2.3
	·1993	·0875	·0871	-1.1				
20.74 ...	...	...	...	...	·3726	·1123	·1165	+4.1
10.37 ...	1.588	·0750	·0796	-0.6	1.878	·1610	·1167	+2.7
Mean ·0892					Mean..... ·1013			
n_1 (corr.) observed ·0937 } ratio					n_1 (corr.) observed ·1040 } ratio			
n_1 " " " ·0742 } 1.26					n_1 " " " ·0819 } 1.27			

be noted that the apparently large divergence for the smallest value of y has really no special significance. At the foot of the table are given the values of n_1 and of n' determined experimentally, reduced to the same date as the values of n_1 in the table. It will be observed that in both cases the calculated value of n_1 is slightly less than the observed, and that in both cases the ratio of the observed value of n_1 to that of n' is the same.

Discussion of the Results.

15. (1) From the identity for gold and for aluminium of the ratio just mentioned, the conclusion may be drawn once more that the number of delta rays excited by a given stream of α rays is the same whether they fall on gold or aluminium.

(2) The calculations have been carried out in such a manner as to throw all errors, whether of experiment or of theory, on the quantity n_1 . Accordingly, the agreement of the calculated values n_1 among themselves and the agreement of the mean with the observed mean is sufficiently satisfactory to afford very convincing proof of the substantial truth of the theory and of the accuracy of the experiments. The difference between the various values of n_1 is almost certainly due to experimental error, for if the values of P from Table XXI. which are calculated with the observed and not the calculated values of μ are taken, this difference is very much

less. But the divergence of the calculated mean from the observed is probably due to deficiencies in the theory. In § 8 of the previous paper it was pointed out that a different value for P would be obtained according as the conditions used in determining the constant of integration were those at $x=0$ or those at $x=b$. The latter have been used; if the former had been used the calculated values of n_1 would have been still smaller; they would have been from 35 per cent. to 40 per cent. of the observed values, and it was this discrepancy which first threw doubts upon the accepted calculations. Now it is almost certain that the error in the theory caused by taking the conditions at $x=b$ is in the same direction, though smaller in amount, than that caused by taking those at $x=0$; and it is therefore to be expected that the calculated values of n_1 should turn out to be slightly too small.

I do not think that anyone will quarrel with the conclusion that Table XXIII. provides as complete a proof as we could possibly hope to attain of the substantial accuracy of the physical assumptions underlying the theory on which the interpretation is based.

16. (3) Accepting this conclusion, we may inquire what light it throws on the various physical problems under discussion.

First, there is the question of which of the two theories discussed in the previous paper, as to the nature of the negative ion after it has made a few collisions, is correct. The results which have been recorded were obtained on the first theory that the electron remains an electron, and does not become a complex ion. How far the results would agree with the second theory cannot be told completely without detailed calculation, but I think a little consideration will show that it is very unlikely that they would agree at all. The values obtained for ν and V' will differ according to the theory adopted, but it is to be noticed that, if the field is so great that every collision results in ionization, the two theories become identical. Adopting the figures for these quantities which we have obtained, we find that, for the largest value of y , the average number of ions made by collision of an electron starting from the electrode is, on the first theory, between 1.3 and 2.5 for the pressures used; while, on the second theory, the number is from 0.6 to 0.7. On the other hand, for the lowest value of y , the same number on the first theory ranges between 0.3 and 1.0, on the second theory it is 0.027. If the same values of ν and V' are applied to both theories for the large value of y , the ionization predicted

by the first theory is about 3 times that predicted by the second; for the small value it is about 20 times. It is very difficult to believe that, even if different values of ν and V' were applied to the two theories, measurements which agree so well with one theory could be made also to agree throughout the whole range of y with another theory, the predictions of which for the same values of ν and V' are so completely different. I think we may conclude with some certainty that the second theory is not correct, and that the formation of complex ions in dry air is not a common event in the life-history of an electron. It is intended in the future to make similar measurements in other gases and vapours to ascertain whether in them the formation of complex ions occurs with greater frequency.

17. (4) The values of ν and V' may be compared with those obtained by Townsend. $N_0 = \frac{\nu}{l}$, and in these experiments l , though not known very accurately, was within 10 per cent. of 0.15. Hence these measurements give

$$N_0 = 12.1, \quad V' = 20.75.$$

Townsend's work gives

$$N_0 = 17.93, \quad V' = 19.00.$$

The difference between the values of N_0 is certainly greater than can be attributed to experimental uncertainties; it is probably due to the deficiencies of the theory. For Townsend used values of l so great that the chance of an electron liberated anywhere between the electrodes reaching the boundary of the field without colliding at all was very small, whereas in my work under the most favourable conditions this chance was as great as 0.16. Further experiments are needed with different values of l to ascertain whether a discrepancy of this nature is to be anticipated from the inadequacy of the mathematical theory.

18. (5) We will now consider what light the agreement between theory and experiment which has been found throws upon our chief question, that of the speed of the delta rays. The theory assumes that the delta rays from both metal and gas have no initial velocity. The assumption that they have such a velocity would alter the theory in two ways. First, the potential difference through which an electron must fall before it acquires the power of ionization would depend on the direction, relatively to that of the field, in which it was ejected. If the initial velocity were small compared with

that which corresponds to V' , it would make little difference to the theory; V' would be an average value for all possible directions of projection. But if the initial velocity were equal to or greater than V' the theory would break down completely; the effect of an electric field would not be to increase ionization, for all the electrons projected in the direction of the field have already the power of making ions at collision, but to decrease it by preventing from ionizing by collision the electrons projected against the field. We may conclude from the agreement between theory and experiment that the delta rays from a gas have not an initial velocity of the order of 20 volts.

Secondly, if the delta rays had an initial velocity of the order of that required to ionize, the rays from the metal would produce more ionization per electron than the rays from the gas; for the rays from the metal only enter the gas if their initial velocity is in the direction in which they fall under the field. Accordingly, when we calculated the number of electrons sent out from the metal from the amount of ionization produced by them on the assumption that they behave like the electrons sent out from the gas, we should obtain too high a value. As a matter of fact we obtain too low a value; the delta rays from the metal appear to produce slightly less, not more, than their fair share of ionization. Again we conclude that the initial velocity of the rays is not of the order of that required to ionize*.

General Conclusions.

19. From all the evidence which has been brought forward in this and the two previous papers we may draw the following conclusions:—

(A) The delta rays have not, as has been supposed, an initial velocity of the order of 20 volts.

(B) If the initial velocity is more than a small fraction of a volt, it is independent of the speed of the exciting alpha rays, and almost, if not quite, independent of the nature of the material in which the delta rays are excited.

(C) The number of delta rays excited by a given beam of alpha rays at a metal surface is independent of the nature of that surface.

* It may be noted that in Townsend's experiments the ions from the electrode, being those due to the photoelectric effect, probably had a small initial velocity. This velocity would only affect the results so far as the first collision is concerned, and, since the electrons made many collisions, its influence is likely to be small. But it may account partly for the fact that Townsend's value for V' is less than my own.

The last conclusion confirms the view that the alpha rays ionize every atom which they pass through, whatever its nature, so long as they have any ionizing power at all—a conclusion which may be deduced from the number of ions made by an alpha particle in travelling through a gas.

From (A) we may conclude that no important part of the energy of ionization appears as energy of the ejected electron. This conclusion appears to me of the utmost importance, for it seems to suggest that the energy expended when gases are ionized is not expended directly in producing ionization, but that it is expended on some other process of which ionization is a bye-product. This view has been already put forward by Prof. Bragg to explain the fact that, whereas the energy expended in ionizing a gas by alpha rays is determined solely by the nature of the atoms in the gas, the amount of ionization produced is not so determined, but depends upon the nature of the molecules in which the atoms are combined; this fact also suggests that the energy does not go directly to producing ionization. The most plausible view seems to be that the energy is expended by the rays in penetrating the atoms through which they pass, and that the ionization is produced by the electrons drifting out of the atoms owing to the internal disturbance of the atom caused by the presence of the alpha particle within it.

(B) suggests very strongly the conclusion that the initial speed of the delta rays is not only small compared with 20 volts, but is actually zero, or at least a very small fraction of a volt. For if this initial velocity is independent of the exciting rays and of the material on which they impinge, on what can it be dependent? Possibly on the temperature of the material, as in the case of free electrons in metals, but then the velocity would only be a small fraction of a volt. The only other physical hypothesis which would lead to a value for the initial velocity universally constant is to the effect that in ionization an “explosive” action of some system common to all atoms is concerned. An hypothesis of this nature has been put forward by J. J. Thomson, but it was based on the view that the actual process of ionization required the expenditure of energy. But we have seen that the experiments are quite consistent with the view that ionization itself requires no energy, that the energy which is spent actually in producing ionization is spent in producing changes in the atom, of which ionization is only a bye-product; it is conceivable that ionization might be produced without any expenditure of energy, even if it is not actually possible so to produce it. (In the case of the free electrons

in a metal, however, it is possible that we have ionization without the expenditure of energy.)

This view that ionization itself requires the expenditure of no energy, and that the initial velocity of the delta ray is zero, or determined merely by the temperature, requires, of course, additional confirmation. But if it can be accepted it may lead to a considerable change in our views in other directions. For instance, most of the difficulties connected with the nature of radiation, which have been the subject of so much discussion lately, appeared originally because, on the old theory of radiation, it was difficult to see whence came the energy which was supposed to be necessary to ionize. If no energy is required to ionize, the difficulties disappear.

But at present there is one piece of experimental evidence, to which reference was made in the second paper on delta rays, which is difficult to reconcile with the hypothesis that the delta rays have no initial velocity. This is the fact that a body emitting delta rays undoubtedly raises itself to a finite positive potential. I am inclined to believe that this action has nothing to do with the emission of delta rays from it; experiments are being undertaken to investigate the matter further, and to discover whether it is as serious an objection to the view that the delta rays have no velocity as appears at present.

Summary.

2-5. Information as to the quantity and quality of delta rays may be obtained by experiments in a gas which they ionize by collision, as well as by experiments in a high vacuum. Some qualitative experiments of this nature are described which lead to the following conclusions:—

(a) There is no difference in the “emergent” and “incident” radiations from the same metal.

(b) The delta rays excited by a given stream of alpha rays in two different metals are the same in quantity and in quality. The conclusion as to quantity is, however, much more certain than the conclusion as to quality.

6. Experiments were next undertaken to investigate the matter more thoroughly by extensive and accurate measurements based on the theory of ionization by collision given in the previous paper.

7-10. The apparatus and the methods of measurement are described, and the numbers obtained given in detail in Tables V.-XIX.

11-15. The method by which the measurements are inter-

puted is described, and the results brought to such a form that they can be compared with theory.

16-18. The results are discussed first with reference to the theory of ionization by collision. It is shown that they afford considerable support for it, if the first of the two alternative theories as to the nature of the negative ion put forward in the previous paper is adopted. They do not seem to agree with the second theory. It is concluded that in dry air an electron remains an electron through most of its career, and that the formation of complex negative ions can only occur rarely if at all.

18. The conclusions to be drawn from the results in the matter of the speed of the delta rays is considered. It is shown that they support the view that the initial speed is small compared with 20 volts.

19. The conclusions concerning delta rays which have been attained in this and two preceding papers are discussed with a view to the light that they throw upon the mechanism of ionization.

It is, of course, clear that the brief discussion given of the mechanism of ionization is largely due to the suggestions of Prof. Bragg, to whose inspiration all this work is due.

Leeds University, Nov. 18, 1911.

XLV. *On the Application of the Theory of Chemical Potential to the Thermodynamical Theory of Solutions.* By S. A. SHORTER, B.Sc., Assistant Lecturer in Physics in the University of Leeds.—Part II. *The Effect of Pressure on Vapour - Pressure. The Vapour - Pressure Theory of Osmotic Pressure. The Freezing of Solutions* *.

IN a previous communication† we considered the equilibrium between the solution and solvent vapour in the case where the surface of separation is plane, and the pressure, therefore, the same in both phases. If the surface of separation is curved, the pressures in the two phases will differ by an amount equal to the product of the surface tension and the total curvature, and the conditions of equilibrium will, of course, be modified. We may also suppose this co-existence of the two phases to be brought about by means of an insoluble gas. This involves the introduction of the idea of partial pressure, as well as the assumption of

* Communicated by the Author.

† Phil. Mag. xxii. p. 933, Dec. 1911. The author takes this opportunity of making the following corrections in Part I.:—page 934, line 17 from top, for S read s: page 938, line 6 from bottom, for $P_0(s, p_0, \theta)$ read $P_0(s, p, \theta)$.

the existence of an insoluble gas. We will therefore confine ourselves to the consideration of the effect of capillary pressure on the vapour-pressure of a solution.

We will also consider the thermodynamical theory of the equilibrium between the solution and solid solvent, and establish exact formulæ connecting the freezing-point with the osmotic pressure and vapour-pressure. These formulæ, which are obviously of fundamental importance in the theory of solutions, appear never to have been previously established.

Some new Symbols used in this Communication.

The following new symbols will be used in the part of the paper dealing with the freezing of solutions. The new symbols used in the earlier parts of the paper will be defined as they occur in the text.

T_0 the freezing-point of the pure solvent under a pressure p ;

T the freezing - point of the solution under a pressure p ;

L_0 the latent heat of fusion of the solid solvent, when in equilibrium with the pure liquid solvent under a pressure p^* ;

$\gamma(s, p, \tau)$ the specific heat of the solution under a constant pressure p , and at a temperature τ ;

$\gamma_0(p, \tau)$ the specific heat (under constant pressure) of the pure liquid solvent ;

$\gamma_s(p, \tau)$ the specific heat (under constant pressure) of the solid solvent ;

$\gamma_d(p, \tau) \equiv \gamma_0(p, \tau) - \gamma_s(p, \tau)$;

$l_0(s, p, \theta)$ the heat of dilution at a pressure p and temperature θ †.

$\phi_0(p, \theta)$ the chemical potential of the solid solvent at a pressure p and temperature θ ;

$\Delta_0(s, p, \theta) \equiv f_0(0, p, \theta) - f_0(s, p, \theta)$;

$\Gamma_0(p, \theta) = \frac{\partial}{\partial \theta} \phi_0(p, \theta) - \frac{\partial}{\partial \theta} f_0(0, p, \theta)$;

$\delta_0(s, p, \theta) \equiv \frac{\partial}{\partial p} \Delta_0(s, p, \theta)$.

* It is unnecessary to adopt the more precise notation $T_0(p)$, $T(s, p)$, $L_0(p)$, as we shall not consider variations of s and p .

† The heat evolved when an infinitesimal mass δM_0 of the solvent is added to the solution (pressure and temperature being maintained constant) is $l_0(s, p, \theta) \delta M_0$.

Dashes will be used to indicate differentiation with respect to the temperature, thus :

$$l'_0(s, p, \theta) = \frac{\partial}{\partial \theta} l_0(s, p, \theta), \phi_0''(p, \theta) = \frac{\partial^2}{\partial \theta^2} \phi_0(p, \theta).$$

The Effect of Pressure on Vapour-Pressure.

If the solution and solvent vapour are in equilibrium, the surface of separation having a curvature such that the pressure of the solution exceeds that of the vapour by an amount p_c , the vapour-pressure Π_c is determined by the equation

$$f_0(s, \Pi_c + p_c, \theta) = F_0(\Pi_c, \theta).$$

When the surface of separation is plane the vapour-pressure Π is determined by the equation

$$f_0(s, \Pi, \theta) = F_0(\Pi, \theta).$$

Hence we have

$$(\Pi_c + p_c - \Pi)P_0(s, \Pi \rightarrow \Pi_c + p_c, \theta) = \int_{\Pi}^{\Pi_c} V(x, \theta) dx. \quad (1)$$

This equation agrees with that obtained in a different manner by Callendar* for the effect of capillary pressure, and with that obtained by Porter† for the effect of the pressure of an insoluble gas.

In the case of the pure solvent, the ordinary vapour-pressure Π_0 and the vapour-pressure Π_{0c} corresponding to a capillary excess pressure p_c , are related by the following equation, which may be derived from equation (1) by putting $s=0$,

$$(\Pi_{0c} + p_c - \Pi_0)v(0, \Pi_0 \rightarrow \Pi_{0c} + p_c, \theta) = \int_{\Pi_0}^{\Pi_{0c}} V(x, \theta) dx. \quad (2)$$

If we neglect the compressibility of the liquid and suppose that the solvent vapour behaves as an ideal gas, we obtain the well-known expression ‡ for the effect of capillary curvature on the vapour-pressure of a liquid.

* Roy. Soc. Proc. A. vol. lxxx. p. 466 (1907).

† Roy. Soc. Proc. A. vol. lxxix. p. 519 (1907).

‡ J. J. Thomson, 'Conduction of Electricity through Gases,' p. 180.

Generalised Vapour-Pressure and the Vapour-Pressure Theory of Osmotic Pressure.

Under ordinary circumstances the solution and solvent vapour when in equilibrium are under the same pressure, so that the vapour-pressure is a function of the concentration and temperature. We have seen, however, that the two phases may co-exist under different pressures. We may therefore generalise the idea of vapour-pressure, and suppose a solution of given concentration at a given temperature to have different vapour-pressures corresponding to different pressures in the solution. The generalised vapour-pressure $\mathbf{P}$ of a solution is determined as a function of the concentration, temperature, and pressure in the solution, by the equation

$$f_0(s, p, \theta) = F_0(\mathbf{P}, \theta) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If we differentiate this equation with respect to the solution pressure, we obtain the equation

$$\frac{\partial \mathbf{P}}{\partial p} = \frac{P_0(s, p, \theta)}{V(\mathbf{P}, \theta)} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

showing the effect of pressure on the generalised vapour-pressure.

Suppose that we have a solution of concentration s_1 under a pressure p_1 in osmotic equilibrium with a solution of concentration s_2 under a pressure p_2 . The generalised vapour-pressures $\mathbf{P}_1$ and $\mathbf{P}_2$ of the two solutions are determined by the equations

$$f_0(s_1, p_1, \theta) = F_0(\mathbf{P}_1, \theta),$$

$$f_0(s_2, p_2, \theta) = F_0(\mathbf{P}_2, \theta).$$

Since the solutions are in osmotic equilibrium we must have

$$f_0(s_1, p_1, \theta) = f_0(s_2, p_2, \theta).$$

Hence we have

$$F_0(\mathbf{P}_1, \theta) = F_0(\mathbf{P}_2, \theta);$$

and therefore, since F_0 always increases with the pressure,

$$\mathbf{P}_1 = \mathbf{P}_2.$$

Hence two solutions in osmotic equilibrium have the same generalised vapour-pressure. The converse of this is obviously true. Two solutions of different concentrations under pressures such that their generalised vapour-pressures are equal will be in osmotic equilibrium under these pressures.

We may therefore regard the osmotic difference of

pressure as the increase of pressure which must be applied to the stronger solution to make its generalised vapour-pressure equal to that of the weaker solution. It seems to me, however, that there is nothing fundamental in this idea. It seems quite a mistake to *define* the osmotic pressure of a solution as the increase of pressure which must be applied to the solution to make its vapour-pressure equal to that of the pure solvent. Thus Callendar's* vapour-pressure theory of osmotic pressure "according to which the osmotic pressure is simply the pressure required to produce equilibrium of vapour-pressure between the solvent and solution" is merely a particular statement of the general thermodynamical truism that the conditions of co-existence of two parts of a system are independent of the precise nature of the mechanism of the co-existence, and depend only on the "constraints" of the mechanism. Callendar's "vapour-sieve" has the same constraint as the semi-permeable membrane—it does not allow the solute to pass from one part of the system to the other. Hence the conditions of equilibrium are the same in the two cases. Whatever may be the nature of the osmotic mechanism, and whatever may be the relation between the magnitude of the osmotic pressure and the composition of the solution, the statement quoted above is true; so it can in no sense be regarded as a theory of osmotic pressure.

The Thermodynamical Theory of the Equilibrium between the Solution and Solid Solvent.

If the pure liquid solvent is in equilibrium with the solid solvent, the temperature T_0 is determined as a function of the pressure only, by the equation

$$f_0(0, p, T_0) = \phi_0(p, T_0) \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If the solution is in equilibrium with the solid solvent, the temperature T is determined as a function of the concentration and pressure by the equation

$$f_0(s, p, T) = \phi_0(p, T) \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Freezing-point determination forms a third method of investigating the thermodynamical properties of solutions. In order to compare the results of such determinations with measurements of the osmotic pressure and vapour-pressure, it is necessary to obtain an expression for the lowering of the chemical potential of the solvent caused by the addition of the solute, similar to those which have been obtained in

* *Loc. cit.*

the cases of osmotic pressure (equation (5) of Part I.) and vapour-pressure (equation (8) of Part I.). The process of obtaining an exact formula is more complicated in the present case than in the two other cases, because we have to deal with variations of temperature, and the temperature derivative of the chemical potential is not connected with quantities which may be determined experimentally in such a simple manner as the pressure derivative.

We will first calculate the lowering of the solvent potential at the freezing-point of the solution. From equations (5) and (6) we obtain

$$f_0(0, p, T_0) - f_0(s, p, T) = \int_T^{T_0} \phi_0'(p, \theta) d\theta,$$

but

$$f_0(0, p, T_0) = f_0(0, p, T) + \int_T^{T_0} f_0'(0, p, \theta) d\theta,$$

so that

$$\Delta_0(s, p, T) = \int_T^{T_0} \Gamma_0(p, \theta) d\theta \quad . \quad . \quad . \quad (7)$$

The value of Γ_0 is known for one value of the temperature, viz., the value T_0 . We have the well-known relation*

$$\Gamma_0(p, T_0) = \frac{L_0}{T_0}.$$

The value of the temperature derivative of Γ_0 is known for any value of the temperature. We have the well-known relations†

$$\tau \phi_0''(p, \tau) = -\gamma_s(p, \tau),$$

$$\tau f_0''(0, p, \tau) = -\gamma_0(p, \tau),$$

so that

$$\Gamma_0'(p, \tau) = \frac{\gamma_s(p, \tau)}{\tau}.$$

The value of Γ_0 at any temperature θ , between T and T_0 , is therefore given by the equation

$$\Gamma_0(p, \theta) = \frac{L_0}{T_0} - \int_{\theta}^{T_0} \frac{\gamma_s(p, \tau)}{\tau} d\tau.$$

* Duhem, *La Mécanique Chimique*, vol. ii. pp. 5 and 54; Preston, 'Theory of Heat,' p. 776 (second edition).

† Duhem, *loc. cit.* vol. i. p. 110; Preston, *loc. cit.* p. 770.

Substituting this value in equation (7), and performing the integration with respect to θ , we obtain the following expression for the lowering of the solvent potential at the freezing-point of the solution :—

$$\Delta_0(s, p, T) = \frac{I_0(T_0 - T)}{T_0} - \int_T^{T_0} \gamma_d(p, \tau) d\tau + T \int_T^{T_0} \frac{\gamma_d(p, \tau)}{\tau} d\tau. \quad (8)$$

The osmotic and vapour-pressure measurements with which the freezing-point determinations have to be compared may have been made at any temperature. It is necessary, therefore, to obtain a formula connecting the potential lowering at two different temperatures. Such a formula is also useful for the comparison of osmotic and vapour-pressure measurements made at different temperatures. We will therefore consider this question in a general manner (apart from its present application) in the next section.

The Variation of the Solvent Potential Lowering with Temperature.

Duhem's expression* for the heat of dilution in terms of the solvent potential lowering may be written in the form

$$\frac{\partial}{\partial \theta} \left\{ \frac{\Delta_0(s, p, \theta)}{\theta} \right\} = - \frac{l_0(s, p, \theta)}{\theta^2}. \quad (9)$$

Hence if θ_1 and θ_2 are any two temperatures we have

$$\frac{\Delta_0(s, p, \theta_2)}{\theta_2} - \frac{\Delta_0(s, p, \theta_1)}{\theta_1} = - \int_{\theta_1}^{\theta_2} \frac{l_0(s, p, \theta)}{\theta^2} d\theta. \quad (10)$$

By combining this equation with equation (8) we could obtain an expression connecting the potential lowering at any temperature with the freezing-point. The equation involves, however, a knowledge of the heat of dilution as a function of the temperature. Now in general the heat of dilution will be known at one temperature only. We will therefore deduce a formula involving a knowledge of the heat of dilution for a single value of the temperature, making use of the well-known expression connecting the temperature derivative of the heat of dilution with specific heat data :

$$l_0'(s, p, \theta) = \gamma_0(p, \theta) - \gamma(s, p, \theta) + s(1 + s) \frac{\partial}{\partial s} \gamma(s, p, \theta). \quad (11)$$

* *Loc. cit.* vol. iii. p. 132.

The value of the heat of dilution at any temperature θ is given, in terms of its value at the temperature θ_0 , by

$$l_0(s, p, \theta) = l_0(s, p, \theta_0) - \int_{\theta}^{\theta_0} l'_0(s, p, \tau) d\tau.$$

Substituting this value in equation (10) and performing the integration with respect to θ , we obtain

$$\begin{aligned} \frac{\Delta_0(s, p, \theta_2)}{\theta_2} - \frac{\Delta_0(s, p, \theta_1)}{\theta_1} \\ = -l_0(s, p, \theta_0) \left(\frac{1}{\theta_1} - \frac{1}{\theta_2} \right) + \frac{1}{\theta_1} \int_{\theta_1}^{\theta_0} l'_0(s, p, \tau) d\tau \\ - \frac{1}{\theta_2} \int_{\theta_2}^{\theta_0} l'_0(s, p, \tau) d\tau - \int_{\theta_1}^{\theta_2} \frac{l'_0(s, p, \tau)}{\tau} d\tau. \quad (12) \end{aligned}$$

This exact formula connecting the values of the solvent potential lowering at two different temperatures may be simplified if we assume that the specific heats involved are independent of the temperature. The equation then reduces to

$$\begin{aligned} \frac{\Delta_0(s, p, \theta_2)}{\theta_2} - \frac{\Delta_0(s, p, \theta_1)}{\theta_1} = -l_0(s, p, \theta_0) \left(\frac{1}{\theta_1} - \frac{1}{\theta_2} \right) \\ + l'_0 \left\{ \frac{\theta_0(\theta_2 - \theta_1)}{\theta_1 \theta_2} - \log \frac{\theta_2}{\theta_1} \right\}. \quad (13) \end{aligned}$$

For the purpose of practical calculation the coefficient of l'_0 may be written in the form

$$\frac{\theta_2 - \theta_1}{\theta_1} \left\{ \frac{\theta_0 - \bar{\theta}}{\theta_2} + \frac{1}{6} \left(\frac{\theta_2 - \theta_1}{\theta_1} \right)^2 - \frac{1}{4} \left(\frac{\theta_2 - \theta_1}{\theta_1} \right)^3 + \dots \right\},$$

where

$$\bar{\theta} = \frac{\theta_1 + \theta_2}{2}.$$

The Relation between the Osmotic Pressure and Vapour-Pressure and the Freezing-Point.

Equations (5) and (8) of Part I. give the value of the solvent potential lowering in terms of the osmotic pressure and vapour-pressure respectively. These two formulæ involve different values of the pressure, but the effect of variations of pressure is easily calculated. Adopting a notation for the mean value of δ_0 similar to that adopted in the case of the function P_0 , we have, if p_1 and p_2 are two

values of the pressure,

$$\Delta_0(s, p_2, \theta) - \Delta_0(s, p_1, \theta) = (p_2 - p_1) \delta_0(s, p_1 \rightarrow p_2, \theta). \quad (14)$$

The mean value of δ_0 is easily calculated. In general, however, the effect of pressure variations is so small that the value of δ_0 corresponding to atmospheric pressure may be used in this formula.

The value, at a pressure p and temperature t , of the solvent potential lowering is given, therefore, in terms of the osmotic pressure at the same temperature, corresponding to a pure solvent pressure p_0 , by the equation

$$\begin{aligned} \Delta_0(s, p, t) = \Omega(s, p_0, t) P_0(s, p_0 \rightarrow p_0 + \Omega, t) \\ + (p - p_0) \delta_0(s, p_0 \rightarrow p, t), \quad . \quad . \quad (15) \end{aligned}$$

and in terms of the vapour-pressure at the same temperature, by the equation

$$\begin{aligned} \Delta_0(s, p, t) = \int_{\Pi}^{\Pi_0} V(x, t) dx - (\Pi_0 - \Pi) P_0(s, \Pi \rightarrow \Pi_0, t) \\ + (p - \Pi_0) \delta_0(s, \Pi_0 \rightarrow p, t). \quad . \quad (16) \end{aligned}$$

Equation (8) gives the value of the solvent potential lowering at the freezing-point of the solution. Calculating the value at the temperature t by means of equation (12) we obtain the formula

$$\begin{aligned} \Delta_0(s, p, t) = L_0 t \left(\frac{1}{T} - \frac{1}{T_0} \right) - \frac{t - T}{T} l_0(s, p, \theta_0) - \frac{t}{T} \int_T^{T_0} \gamma_d(p, \tau) d\tau \\ + t \int_T^{T_0} \frac{\gamma_d(p, \tau)}{\tau} d\tau + \frac{t}{T} \int_T^{\theta_0} l'_0(s, p, \tau) d\tau \\ - \int_t^{\theta_0} l'_0(s, p, \tau) d\tau - t \int_T^t \frac{l'_0(s, p, \tau)}{\tau} d\tau. \quad . \quad (17) \end{aligned}$$

Equations (15) and (17) give an exact relation between the osmotic pressure and the freezing-point, and equations (16) and (17) an exact relation between the vapour-pressure and the freezing-point. By combining equations (15) and (16) we obtain the equation connecting vapour-pressure and osmotic pressure deduced in a slightly different manner in Part I.

In the next section we will simplify these relations by making various approximations and compare the results thus obtained with expressions deduced by other investigators.

Approximate Expressions connecting the Freezing-Point with the Solvent Potential Lowering, Osmotic Pressure, and Vapour-Pressure.

If we regard all the specific heats involved in equation (17) as independent of the temperature, the equation reduces to the simpler form

$$\Delta_0(s, p, t) = L_0 t \left(\frac{1}{T} - \frac{1}{T_0} \right) - \frac{t-T}{T} l_0(s, p, \theta_0) - \gamma_{dt} \left(\frac{T_0-T}{T} - \log \frac{T_0}{T} \right) + l'_0 t \left\{ \frac{\theta_0(t-T)}{Tt} - \log \frac{t}{T} \right\}. \quad (18)$$

For the purpose of practical calculation, the equation may be written in the form

$$\begin{aligned} \Delta_0(s, p, t) = L_0 t \left(\frac{1}{T} - \frac{1}{T_0} \right) - \frac{t-T}{T} l_0(s, p, \theta_0) \\ - \gamma_{dt} \left\{ \frac{1}{2} \left(\frac{T_0-T}{T} \right)^2 - \frac{1}{3} \left(\frac{T_0-T}{T} \right)^3 + \dots \right\} \\ + \frac{l'_0 t(t-T)}{T} \left\{ \frac{\theta_0 - \bar{\theta}}{t} + \frac{1}{6} \left(\frac{t-T}{T} \right)^2 - \dots \right\}, \quad (19) \end{aligned}$$

where

$$\bar{\theta} = \frac{t+T}{2}.$$

The relation between the osmotic pressure and the freezing-point may be simplified in the following manner. Let us suppose that the pure solvent in the case of the osmotic pressure measurements, and the solution in the case of the freezing-point determinations, are both under atmospheric pressure. We may express the mean value of P_0 in terms of its value at atmospheric pressure by means of equation (2) of Part I. Simplifying equation (15) in this manner and combining it with equation (19) we obtain the following relation * :—

$$\begin{aligned} \Omega(s, \varpi, t) P_0(s, \varpi, t) (1 - \frac{1}{2} \lambda \Omega) = L_0 t \left(\frac{1}{T} - \frac{1}{T_0} \right) \\ - \frac{t-T}{T} l_0(s, \varpi, \theta_0) - \gamma_{dt} \left\{ \frac{1}{2} \left(\frac{T_0-T}{T} \right)^2 - \frac{1}{3} \left(\frac{T_0-T}{T} \right)^3 + \dots \right\} \\ + \frac{l'_0 t(t-T)}{T} \left\{ \frac{\theta_0 - \bar{\theta}}{t} + \frac{1}{6} \left(\frac{t-T}{T} \right)^2 - \dots \right\}. \quad (20) \end{aligned}$$

* It is quite justifiable to take account of the compressibility and at the same time neglect the variation with temperature of the specific heats.

If in the above equation we make $\theta_0 = t$, and neglect the compressibility and powers of $T_0 - T$ and $t - T$ higher than the second, we obtain Ewan's expression * connecting the osmotic pressure and the freezing-point.

In the absence of any information regarding the precise form of the isothermal of the solvent vapour, the definite integral in equation (16) must be evaluated on the assumption that the solvent vapour behaves as an ideal gas, *i. e.*, we must assume that

$$\int_{\Pi}^{\Pi_0} V(x, t) dx = R_0 t \log \frac{\Pi_0}{\Pi}, \dots \dots (21)$$

where R_0 is the "gas constant" of the solvent vapour. If we make this assumption we must, of course, neglect the term $(\Pi_0 - \Pi)P_0$. The magnitude of the third term on the right-hand side of equation (16) will depend upon several factors. Speaking generally, we may say that its retention in the equation is justifiable only in the case of strong solutions at low temperatures (when δ_0 is a fairly large fraction of the specific volume of the pure solvent, and $\Pi_0 - \Pi$ only a small fraction of $p - \Pi_0$). Making these approximations and putting $p = \varpi$, we obtain the following expression connecting the vapour-pressure and the freezing-point:—

$$\begin{aligned} R_0 t \log \frac{\Pi_0}{\Pi} + (\varpi - \Pi_0) \delta_0(s, \varpi, t) &= L_0 t \left(\frac{1}{T} - \frac{1}{T_0} \right) \\ &- \frac{t - T}{T} l_0(s, \varpi, \theta_0) - \gamma_{at} \left\{ \frac{1}{2} \left(\frac{T_0 - T}{T} \right)^2 - \frac{1}{3} \left(\frac{T_0 - T}{T} \right)^3 + \dots \right\} \\ &+ \frac{l_0' t (t - T)}{T} \left\{ \frac{\theta_0 - \bar{\theta}}{t} + \frac{1}{6} \left(\frac{t - T}{t} \right)^2 - \dots \right\}. \dots \dots (22) \end{aligned}$$

If we make $t = T_0$, and neglect the terms containing δ_0 and l_0' , we obtain Dieterici's † equation connecting the freezing-point of the solution with the vapour-pressure at the pure solvent freezing-point.

If we substitute in equation (8) the approximate value of the potential lowering calculated as in equation (21) we obtain Callendar's ‡ expression for the ratio of the vapour-pressures of the pure solvent and solution at the freezing-point of the latter.

The simplest method of comparing a large number of experimental data relating to a particular solution is to calculate the value of the solvent potential lowering at some

* *Zeit. für Phys. Chem.* xxxi. p. 22 (1899).

† *Wied. Ann.* lii. p. 263 (1894).

‡ *Loc. cit.*

standard pressure and temperature. By means of the formulæ established in this work this may be done to a degree of accuracy limited only by the accuracy of the experimental data. The writer hopes to publish some examples of such a comparison at a later date.

The third (and last) part of the present work will deal with the effect of gravity on a solution, and the extension of the theory to the case of a solution containing any number of involatile solutes.

The University, Leeds,
Dec. 23, 1911.

XLVI. *A New Approach to the Theory of Relativity.* By
EDWARD V. HUNTINGTON, Ph.D., Assistant Professor of
Mathematics in Harvard University*.

INTRODUCTION.

I. SYSTEM AT REST IN THE ÆTHER.

The regulating and setting of stationary clocks.
Laying out a system of coordinates by light signals.
Definition of distance.
Definition of observed velocity.
Definition of observed rate of a moving clock.
Doppler's principle.

II. SYSTEM IN UNIFORM MOTION THROUGH THE ÆTHER.

The transformation equations.
Features of the moving system.
The composition of velocities.

III. THE PRINCIPLE OF RELATIVITY.

The inverse transformation equations.
Experiments in which no observer leaves his own station.
Experiments with a portable measuring-rod; first physical assumption involved in the theory of relativity.
Experiments with a portable clock; second physical assumption involved in the theory of relativity.

APPENDIX.

INTRODUCTION.

THE Theory of Relativity as developed by Einstein † is usually supposed to involve a radical modification, not only of our conception of the æther, but also of our fundamental notions concerning space and time; and the discussion of the so-called "paradoxes of relativity" has

* Communicated by the Author. Reprinted from the *Heinrich Weber Festschrift* (Teubner, 1912).

† A. Einstein, "Zur elektrodynamik bewegter Körper," *Annalen der Physik*, ser. 4, vol. xvii. pp. 891-921 (1905).

often led beyond the safe ground of mathematical deduction into the realms of metaphysical speculation.

The purpose of this article is to show that the famous "transformation equations" which stand at the centre of the theory can be easily deduced from simple conventions in regard to the *setting of clocks* and the *laying out of coordinate systems*, without any conflict with our ordinary conception of the æther, or with our ordinary notions of space and time, thereby *freeing the theory from the least appearance of paradox*.

The method pursued is in some sense a return to the point of view of Lorentz *, who retained the concept of the æther as his starting point, and never abandoned our ordinary notions of time and space; and the "transformation equations" here obtained resemble the equations of Lorentz in being slightly more general than those of Einstein. Lorentz's method of deducing these equations, however, involves a large and difficult part of the modern electromagnetic theory, while the method here adopted depends only on the most elementary considerations.

The present article is purely expository, and does not attempt any critical or historical discussion †.

I. SYSTEM AT REST IN THE ÆTHER.

1. We assume an æther in which light-waves are propagated uniformly in all directions, and we consider first a rigid platform, S, at rest in the æther.

This platform is supposed to be inhabited by intelligent beings, who are able to communicate with one another, but are not supposed to be capable of locomotion; that is, *no observer is to leave his own station*. Each station is provided with a clock, that is, any mechanical contrivance which "clicks" at regular intervals. These clocks are not portable, and they must be "regulated" and "set" before they can be used.

We proceed to define methods by which such beings may regulate and set their clocks, lay out a system of coordinates, and develop the entire theory of analytical geometry and

* H. A. Lorentz, 'Versuch einer Theorie der elektrischen und optischen Erscheinungen in bewegten Körpern,' Leiden, 1895. Neudruck, Leipzig, 1906. Also, "The Theory of Electrons" (Columbia University Lectures, 1906), Leipzig, 1909.

† For an extensive bibliography of the "Theory of Relativity," the reader is referred to an article by J. Laub, in the *Jahrbuch der Radioaktivität und Elektronik*, vol. vii. p. 405, December 1910.

kinematics without any observer's leaving his own station. These definitions will then be capable of immediate extension to the case of a system in uniform motion through the æther.

The regulating and setting of stationary clocks.

2. To test whether the clock at any given station A is running at a uniform rate, the observers proceed as follows: a light-signal is sent from A to any second station B, and immediately returned from B to A; if the number of seconds ticked off by the clock at A while the light-signal is making its round trip to B and return is always the same whenever the experiment is repeated, then the clock at A is said to be running at a *constant rate*.

3. Each separate clock being regulated to run at a *constant rate*, the next thing to do is to see that all the clocks run at the *same rate*. This may be easily accomplished by regulating all the clocks so as to agree with a standard clock in some central station O, as follows. Light-signals are sent out from O, at a certain rate per second as measured by the clock at O; if these arrive at station A at the same rate per second as measured by the clock at A, then the clock at A is said to be *running at the same rate as the clock at O*.

Now it is obviously possible for two clocks to be running at the same rate without being synchronous. For example (supposing for convenience that the clocks read continuously 0, 1, 2, . . . seconds, instead of from 12 o'clock around to 12 again), we may have two clocks side by side, one reading

.... 7, 8, 9, 10, ...

while the other reads

.... 3, 4, 5, 6, ...

These clocks are running at the same rate, but they are clearly not synchronous, since the one is always four seconds ahead of the other.

4. It remains, therefore, to "set" the clocks so that they shall all be synchronous—in other words, so that the "origin of time" shall be the same for all. This may be readily accomplished by light-signals from the central station*. Let the observer at O start a signal towards A when the clock at O reads t_0 , and suppose this signal arrives at A when the clock at A reads t_1 ; immediately on the receipt of this signal, the observer at A starts a return signal back towards O, which arrives at O when the clock at O reads t_2 .

* Einstein, *loc. cit.*

If now

$$t_1 = \frac{1}{2}(t_2 + t_0), \quad \text{so that} \quad t_2 - t_1 = t_1 - t_0,$$

then the clock at A is said to be *synchronous with the standard clock at O* *.

It follows as a theorem that two clocks which are synchronous with the clock at O will be synchronous, by the same definition, with each other.

Laying out a system of coordinates by light signals.

5. All the clocks being now properly “regulated,” and “set” so as to be synchronous with the central clock at O, the observers proceed to lay out a *system of coordinates*—that is, to assign to each station a pair of numbers to be called the abscissa and ordinate of that station.

Since no observer is supposed to move from his own station, the ordinary process of measurement, by carrying a metre-stick about from place to place, is not practicable; hence the observers resort to a further use of the method of light-signals, as follows. A fixed line OX through the central station being taken as the axis of x , light-signals are sent from O to the various stations along this axis. If a signal which starts from O when the clock at O reads t_0 arrives at A when the clock at A reads t_1 , then the *difference in clock-readings, multiplied by a constant numerical factor c , is taken as the abscissa of the station A*,

$$x = c(t_1 - t_0);$$

and the point A is denoted by $(x, 0)$ †. In this way the points $(1, 0)$, $(2, 0)$, &c. on OX are determined, and similarly, the points $(-1, 0)$, $(-2, 0)$, &c. on the extension of OX through O.

6. Having thus assigned coordinates to all the stations on the axis of x , the observers now determine—still without any ordinary measurements—the coordinates of points not on the axis of x . Consider any point $(m, 0)$ on the axis. Observers at two points $(m+n, 0)$ and $(m-n, 0)$, which may be called “equidistant” from $(m, 0)$, send out light-signals, each observer starting his signal when the clock at his station reads t_0 . *Any station C at which these two signals*

* If $t_1 = \frac{1}{2}(t_2 + t_0) + e$, then the clock at A is e seconds too fast, and must be “set back” accordingly.

† The arbitrary constant c merely determines the scale on which the map is laid out.

arrive simultaneously is said to lie on the perpendicular through $(m, 0)$. To each of the points that lie on this perpendicular an ordinate, y , is now assigned in an obvious way, by means of light-signals started from the point $(m, 0)$. In particular, the points $(m, 1)$, $(m, 2)$, ...; $(m, -1)$, $(m, -2)$, ... are determined.

7. In describing this rather novel process of laying out a coordinate system by light-signals, we have tacitly assumed that each stage of the process is possible—in other words, that the coordinate system thus obtained will be *permanent*, so that the coordinates assigned to any given station will always be the same whenever the process is repeated. This assumption is obviously justified in the case of a system at rest in the æther; but a moment's reflexion will show that this will not in general be true in the case of a system which is moving with respect to the æther.

For example, consider a circular platform rotating with constant velocity about its centre O. Here all the clocks could readily be synchronized with a central clock at O, according to the rule in § 4; but two clocks A and B on the circumference would then *not* be synchronous with each other according to the same rule*.

In one special case, however, the process is legitimate, namely, in case of a *system moving through the æther with uniform velocity in a straight line*, and to the proof of this we shall turn our attention in Part II. For the present, we consider only the case of a system at rest.

Definition of distance.

8. A pair of coordinates having been assigned by the method of light-signals to every station in the plane, the "distance" between two points (x_1, y_1) and (x_2, y_2) is then defined as the quantity

$$\sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2},$$

and the observers on the platform are now in a position to develop the whole theory of *coordinate geometry for the plane*. For example, all points whose coordinates were found to satisfy the equation $x^2 + y^2 = r^2$ would be said to lie on a circle of radius r , &c.

Definition of observed velocity.

9. The observers are now able to discuss the *velocity* of an object, say an aeroplane, that flies in a straight line across their platform. To determine the velocity, two observers

* The relation "synchronous with," as here defined, is therefore, although symmetrical, not necessarily transitive; it resembles rather the relation "friend of." A and B may both be friends of C, and yet not be friends of each other.

are required, each with his own clock. Observer A, at (x_1, y_1) , notes that the aeroplane passes his station when his clock reads t_1 ; observer B, at (x_2, y_2) , notes that it passes his station when his clock reads t_2 ; then the ratio of "distance" divided by "difference in clock-readings" (supposing this ratio to be constant for any two observers in the line of flight) is called the *observed velocity* of the aeroplane with respect to the platform :

$$u = \frac{\sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2}}{t_2 - t_1} *.$$

In particular, the *velocity of a light-signal*, as determined in this way, is equal to the arbitrarily chosen constant c , and is the same in all directions.

(That this is true for light travelling along the axis of x , or along a line perpendicular to that axis, is obvious from the way in which the coordinates of points on those lines were assigned; that it is true also for light travelling in oblique directions follows readily from the definition of distance in § 8.)

Definition of observed rate of a moving clock.

10. Let us now suppose an aviator, flying across the platform, carries a clock with him, and let

t_1 = the reading of the clock at A when the aviator passes A ;

t_2 = the reading of the clock at B when the aviator passes B ;

and T' = the number of seconds ticked off by the clock on the aeroplane during the flight from A to B.

Then the ratio

$$r = \frac{T'}{t_2 - t_1}$$

(if this ratio proves to be constant) is called the *observed rate* at which the clock on the aeroplane is running with respect to the clocks on the platform; that is, the clock on the aeroplane is said to be running r times as fast as the clocks on the platform.

* The extension of this definition to cases where the velocity is not constant is effected in the usual manner, by the methods of the differential calculus.

Further, the quantity

$$n = \frac{AB}{T'},$$

where AB = the distance over which the aviator passes in the time-interval T' , may be called the *self-measured velocity* of the aeroplane with respect to the platform S , since the time interval T' is measured, not by two clocks on the platform S , but by the single clock on the aeroplane.

The relation between the quantities u and n is as follows :

If

u = the observed velocity of the aeroplane

and

n = its self-measured velocity,

then

$$\frac{u}{n} = r,$$

where r = the observed rate of the clock on the aeroplane.

Doppler's Principle.

11. Suppose an aviator is flying in a straight line away from a given station A , and let light-signals, sent out from A at intervals of T seconds as measured by the clock at A , overtake the aviator at intervals of T' seconds as measured by the clock on the aeroplane. Then we readily find that

$$T' = \frac{T}{\frac{n}{u} - \frac{n}{c}}, \quad \text{or} \quad T' = \frac{rT}{1 - \frac{u}{c}},$$

where u = the observed velocity of the aviator, n = his self-measured velocity, and r = the observed rate of his clock.

This equation reduces to the common form when $r=1$, and to the form given by Einstein when $r = \sqrt{1 - (u/c)^2}$.

In all this discussion we have supposed that the platform S is at rest in the æther. We now turn to the consideration of the case of a platform in motion through the æther.

II. SYSTEM IN UNIFORM MOTION THROUGH THE ÆTHER.

12. We consider a platform S' moving with respect to our stationary platform S with a constant observed velocity v in a straight line, and we proceed to show that the observers on the moving platform S' , having established a central clock at O' , can lay out a permanent system of coordinates on S' by

exactly the same method as that already described for the stationary platform S, provided only that $v < c^*$.

The method of proof will be as follows: we shall first suppose the coordinates on S' to be theoretically assigned by means of certain transformation equations; we shall then show that the result of this assignment is precisely the same as if the observers had used the method of light-signals described above. Since the theoretical method of assignment is easily seen to be possible and permanent, it follows that the method of light-signals is also possible and permanent.

We suppose for convenience that the axis O'X' on S' is sliding along OX in the positive direction; and we suppose that at the instant when O' is opposite O, the clocks at O and O' read zero seconds.

We shall not, however, place any restriction on the observed rate, r , of the clock at O' †.

The transformation equations.

13. We now state the following theorem, which is fundamental for the whole discussion.

THEOREM 1. *If the coordinates x', y' and the clock-reading t' at each station on the moving platform S' are assigned, at each instant, in terms of the coordinates x, y and the clock-reading t at the point on S which is opposite that station at that instant, according to the following "transformation equations":*

$$x' = lk(x - vt), \quad y' = ly, \quad t' = lk\left(t - \frac{v}{c^2}x\right),$$

where

$$k = \frac{1}{\sqrt{1 - (v/c)^2}} \quad \text{and} \quad l = \frac{r}{\sqrt{1 - (v/c)^2}},$$

then the result will be precisely the same as if the observers on S' had adjusted their clocks and laid out their coordinate system

* This restriction does not mean that "no velocity greater than the velocity of light is possible," since an "observed velocity" as here defined may have *any* value from 0 to ∞ ; it means simply that if a platform S' were moving through the æther with a velocity greater than the velocity of light, then the "method of light-signals" here described could not be successfully employed by observers on that platform.

† This feature of our treatment is believed to be new. Einstein, for example, assumes that the two sets of clocks are "of the same physical construction."

by the method of light-signals explained above for platform S, with the same choice of the constant c^* .

Here v = the observed velocity of the point O' with respect to the platform S, and r = the observed rate of the clock at O' .

In order to establish this theorem we must show :—

- (1) that the coordinates x', y' assigned to any given station will be permanent, that is, independent of the time $\dagger$;

and further, that if x', y' , and t' are assigned in the manner indicated, then

- (2) the clock at O' will be found to run at a uniform rate according to the test laid down in § 2 ;
- (3) each clock on S' will be found to be synchronous with the clock at O' according to the test laid down in §§ 3-4 ; and
- (4) if a light-signal, started from O' when the clock at O' reads t_0' , arrives at any station $A' = (x', y')$ when the clock at A' reads t_1' , then the "distance" $\sqrt{x'^2 + y'^2}$ from O' to A' is c times the "difference in clock-readings" $t_1' - t_0'$.

The verification of the truth of these statements is merely a matter of direct computation from the transformation equations, which may well be left to the reader $\ddagger$.

* The expression for k in the above formulas can be simplified by the use of hyperbolic functions. Thus, if we determine a quantity V so that

$$\frac{v}{c} = \tanh V,$$

then

$$k = \cosh V.$$

Further, by a particular assumption in regard to the rate at which the clock at O' is running, the value of l can be reduced to unity. But for the theorems which we shall give, this assumption is not necessary, and will not be made.

The notation, k, l , here used, agrees with the notation of Lorentz rather than with that of Einstein, who uses β in place of k , and has $l = 1$.

$\dagger$ Thus, if a given station on S' is opposite A_1 when the clock A_1 reads t_1 and, later, is opposite A_2 when the clock at A_2 reads t_2 , then the " t " in the formula for x' will have increased by $t_2 - t_1$, while (since the station in question is passing platform S with velocity v) the " x " in that formula will have increased by $v(t_2 - t_1)$; hence the value of $x - vt$ will remain unchanged.

$\ddagger$ The method by which the transformation equations themselves are obtained will be explained in the appendix.

14. By this Theorem 1, the possibility of laying out a permanent set of coordinates on the moving system S' by the method of light-signals is established; the definitions of distance and velocity given for the stationary system S can then be applied directly to the moving system S' , and the theory of analytical geometry and kinematics developed by the residents on S' will be identical with the theory developed by the residents on S .

In particular, the velocity of a light-signal, as computed by two observers on S' , will be found to be constant and the same in all directions, in spite of the fact that the platform is moving through the æther. This proposition, which here follows quite naturally from the way in which the coordinates were laid out on the moving system, appears in Einstein's treatment as a fundamental hypothesis, and is known as the famous "second postulate of relativity."

Features of the moving system.

15. In order to show in detail how the coordinate system thus laid out on the moving platform will appear to observers on the stationary platform, we state the two following theorems, both of which can be deduced by a simple calculation from the transformation equations in § 13.

DEFINITION. Suppose a number of observers, $A, B, C, \dots$ on S agree to observe the points opposite them "at a specified time"—that is, each one is to make his observation when his own clock reads, say, t_0 . Let A' be the point opposite A when A 's clock reads t_0 , B' the point opposite B when B 's clock reads t_0 , &c. Then the figure formed by $A, B, C, \dots$ in S is called the *image in S* of the figure formed by $A', B', C', \dots$ in S' .

THEOREM 2. Consider one of the "townships" $A' B' C' D'$ into which the platform S' is divided by its coordinate network; and let $A B C D$ be the "image in S " of this township. Then $A' B' C' D'$, when computed by the coordinates in S' , is a square; but $A B C D$, when computed by the coordinates in S , is a rectangle, with its short side lying in the direction of the motion of S' . The ratio of the sides is given by

$$\frac{\text{longitudinal side}}{\text{transverse side}} = \sqrt{1 - \frac{v^2}{c^2}} = \frac{1}{k}.$$

It should be noticed that this ratio depends only on the velocity v , and not on the relative rates of the clocks at O and O' .

COROLLARY. If a series of points in S' lie on a *circle*, according to the observers on S' , their images in S will appear to observers in S to lie on an *ellipse*, the minor axis lying in the direction of motion, and the ratio of the axes being $1/k$.

16. THEOREM 3. Let two observers, A and B, on S agree to observe the coordinates and the clock-readings at the points of S' which are opposite them "at a specified time." Suppose when A's clock reads t_0 , the point opposite A has an abscissa $=x_1'$ and a clock-reading $=t_1'$; and when B's clock reads t_0 , the point opposite B has an abscissa $=x_2'$ and a clock-reading $=t_2'$. Then it will appear that

$$t_2' - t_1' = -\frac{v}{c^2}(x_2' - x_1').$$

This theorem tells us that two clocks on S' which are synchronous when tested by the standards adopted on S' , are not synchronous when observed from S —the forward clock being slower than the other by an amount proportional to the distance between them.—This result, like the last, is entirely independent of the relative rates of the clocks at O and O'.

The composition of velocities.

17. Further, we suppose that an aeroplane passes over platform S with a given observed velocity u , and inquire what the observed velocity of the aeroplane will be with respect to platform S' . For simplicity we confine ourselves to the case of motion in a straight line parallel to the line of motion of the platform S' .

THEOREM 4. *If u = the observed velocity of the aeroplane as computed by two observers on S , and u' = its observed velocity as computed by two observers on S' , then*

$$u' = \frac{u-v}{1 - \frac{uv}{c^2}},$$

provided the aeroplane is flying in a line parallel to the axis of x .

Here again we notice that this relation is entirely independent of the relative rates of the central clocks at O and O'.

This relation between u' and u can be expressed much more compactly by the use of hyperbolic functions. Thus, if we determine U , U' , and V so that

$$\frac{u}{c} = \tanh U, \quad \frac{u'}{c} = \tanh U', \quad \text{and} \quad \frac{v}{c} = \tanh V,$$

then the relation in question becomes simply

$$U' = U - V.$$

18. Finally, suppose the aviator flying over the platform carries a clock, the observed rate of which with respect to S is R , and let us inquire what the observed rate of the clock will be with respect to S .

THEOREM 5.

If u = observed velocity of the aviator with respect to S,
 u' = " " " " " " " " S',
 R = observed rate of the aviator's clock with respect to S,
 and R' = " " " " " " " " S',
 then
$$\frac{R'}{\sqrt{1-(u'/c)^2}} = \frac{R}{\sqrt{1-(u/c)^2}} \div \frac{r}{\sqrt{1-(v/c)^2}},$$

where v = observed velocity of O' and r = observed rate of the clock at O', with respect to S.

All these theorems, strange as they may seem at first sight, are readily proved from the transformation equations in Theorem 1.

III. THE PRINCIPLE OF RELATIVITY.

19. We have now shown how observers on our moving platform S' can regulate their clocks and lay out a permanent system of coordinates, by the method of light-signals, and we have shown how this system will appear to observers on a stationary platform.

We now proceed to inquire to what extent this system S' conforms to the Principle of Relativity.

20. The guiding principle of the Theory of Relativity may be stated as follows :

Observers on a system which is moving with uniform velocity through the ether can never detect that motion by any observations which they can make.

In order to ascertain to what extent our system S' conforms to this principle, we now inquire whether there are any kinematical experiments that the observers on S' can make, the results of which will be distinguishable from the results of similar experiments performed by observers on S.

We shall consider first the experiments which can be made without any observer's leaving his own station ; secondly, the experiments which can be made by the aid of a portable measuring-rod ; and thirdly, the experiments which can be made by the aid of a portable clock *.

We begin by obtaining the inverse transformation equations, by which we may determine how the stationary system S will appear to observers on the moving system S'.

* Dynamical experiments, involving the notion of mass, can be treated in a similar way, but are not considered in the present paper, on account of lack of space.

The inverse transformation equations.

21. Let v = the observed velocity of O' as computed by two observers on S , and v' = the observed velocity of O as computed by two observers on S' .

Then we find :—

LEMMA 1. *The observed velocities v and v' will always be equal and of opposite sign :*

$$v' = -v,$$

whatever the relative rates of the central clocks at O and O' .

Further, let r = the observed rate of the clock at O' with respect to S , and r' = the observed rate of the clock at O with respect to S' (see § 10).

Then :—

LEMMA 2. *The numbers r and r' are connected by the relation*

$$rr' = 1 - \frac{v^2}{c^2}.$$

22. By solving the equations in Theorem 1 for x , y , and t , and using the results of these lemmas, we obtain the following theorem :

THEOREM 6. *The “inverse transformations” by means of which, when the coordinates x' , y' , and the time t' at any point on S' are known, the coordinates x , y , and the time t of the opposite point on S may be determined, are as follows :*

$$x = l'k(x' - v't'), \quad y = l'y',$$

$$t = l'k\left(t' - \frac{v'}{c^2}x'\right),$$

where

$$v' = -v, \quad k = \frac{1}{\sqrt{1 - (v/c)^2}}, \quad \text{and} \quad l' = \frac{r'}{\sqrt{1 - (v/c)^2}}.$$

These equations are of exactly the same form as the equations in Theorem 1, if we interchange the accented and unaccented letters.

Experiments in which no observer leaves his own station.

23. These equations in Theorem 6 show that if the observers on S' are not allowed to leave their several stations, the system S' *does* obey the Principle of Relativity; for the symmetry of these equations shows that, if we confine ourselves to the kind of observations so far considered, the observers on S' have as much right as the observers on S to suppose that their platform is at rest in the æther.

In particular, *the results stated in Theorems 2, 3, and 4 will still hold true if we interchange S and S' in the statements of those theorems*—the relations between the two systems being entirely reciprocal. Put briefly, a figure in *either* system appears to be shortened in the direction of motion when observed from the other system; and if two synchronized clocks on *either* system are observed from the other system, the one which seems to be in front in space appears to be behind in time. These are the famous *paradoxes of the Theory of Relativity*, which are often cited as proof of the assertion that the Theory of Relativity is incompatible with our ordinary ideas of time and space, but which here appear as necessary consequences of perfectly natural and reasonable conventions for setting clocks and laying out coordinates.

24. In order to emphasize this result still further, and to show how completely the æther drops out of the calculation, we shall now consider *two* moving platforms, S' and S'', and write out explicitly the transformation equations that hold between them. The method will be the obvious one of writing the transformation equations connecting each of the systems S' and S'' with the stationary system S, and then eliminating S.

Let v' , v'' = the velocities of O' and O'' with respect to S, and put

$$\frac{v'}{c} = \tanh V' \quad \text{and} \quad \frac{v''}{c} = \tanh V''$$

$$\text{so that } k' = \frac{1}{\sqrt{1-(v'/c)^2}} = \cosh V' \quad \text{and} \quad k'' = \frac{1}{\sqrt{1-(v''/c)^2}} = \cosh V''.$$

Further, let r' , r'' = the observed rates of the clocks at O' and O'' with respect to S, and put

$$l' = \frac{r'}{\sqrt{1-(v'/c)^2}} \quad \text{and} \quad l'' = \frac{r''}{\sqrt{1-(v''/c)^2}}.$$

These are the quantities which enter the equations connecting S' and S'' with S, by Theorem 1.

Now let v = the *observed velocity of S'' with respect to S'*, and put $\frac{v}{c} = \tanh V$, so that

$$k = \frac{1}{\sqrt{1-(v/c)^2}} = \cosh V;$$

also let r = the *observed rate of the clock at O'' with respect to S'*

$$\text{and put } l = \frac{r}{\sqrt{1-(v/c)^2}}.$$

Then a perfectly straightforward, though somewhat long, calculation gives us the following theorem

THEOREM 7. The transformation equations which give x'', y'', t'' at any point of S'' in terms of the x', y', t' at the opposite point on S' are

$$x'' = lk(x' - vt'), \quad y'' = ly',$$

$$t'' = lk(t' - \frac{v}{c^2} x'),$$

where

$$V = V'' - V',$$

and

$$l = \frac{l''}{\gamma}.$$

As was to be expected, these equations are of precisely the same form as those in Theorem 1.

All these equations are somewhat simplified if the clocks at O' and O'' are so regulated that

$$r' = \sqrt{1 - (v'/c)^2} \quad \text{and} \quad r'' = \sqrt{1 - (v''/c)^2},$$

in which case all the l 's become unity. It is in this simplified form that the equations are given by Einstein.

We have thus shown that as far as experiments of the first type (§ 20) are concerned, the Principle of Relativity is satisfied by our system S' .

Experiments with a portable measuring-rod : first physical assumption involved in the Theory of Relativity.

25. We now suppose that the observers on S' are provided with a *portable measuring-rod*, with which they can "measure," for example, the adjacent sides $A'B'$ and $B'C'$ of one of the townships $A'B'C'D'$ into which the platform S' is divided by its coordinate network ; and we inquire whether this process of measurement will enable the observers to detect the motion of their platform S' through the æther. (It must be remembered that the coordinate network has been laid out, not by ordinary measurements, but by the method of light-signals explained above.)

26. DEFINITION. The *observed length* of a rod MN with respect to a platform S' is the distance (§ 8) between the points M' and N' , where M' and N' are the "images" (§ 15) of M and N in S' . The *absolute length* of the rod is its "observed length" taken with respect to a platform S which is at rest in the æther.

Now there are two assumptions which we can make in regard to the behaviour of the rod when moving through the æther.

If we assume that the absolute length of the rod is the same whether the rod be moving lengthwise or sideways through the æther, then by Theorem 2, a rod which just fits the side $A'B'$ of our "township" would *not* fit the side $B'C'$ unless the platform were at rest in the æther, and the

observers could by this experiment determine whether or not their system is in motion.

If, on the other hand, we assume with Lorentz that the absolute length of the rod when moving lengthwise is less than it is when moving sidewise (and by the proper amount), then a rod which fits $A'B'$ would also fit $B'C'$, and in this case the experiment would give no information as to whether the platform is in motion through the æther or not.

27. If we desire, therefore, that our system S' shall conform to the Principle of Relativity, we must make the following assumption, which was first suggested by Lorentz in 1895 :

ASSUMPTION A. *The "absolute length" of a material rod (see § 26) moving through the æther with velocity v , is less when the rod is moving lengthwise than it is when the rod is moving sidewise, the ratio of the lengths being*

$$\frac{1}{\sqrt{1-(v/c)^2}},$$

where c is the observed velocity of light.

28. If this assumption is true, we can then deduce the following remarkable theorem, in which S' is any platform, moving with constant velocity through the æther, on which a system of coordinates has been laid out by the method of light-signals :

THEOREM 8. *If Assumption A is true, the "observed length" of a material rod moving with an observed velocity u' with respect to platform S' is less when the rod is moving lengthwise than it is when the rod is moving sidewise—the ratio of the lengths being*

$$\frac{1}{\sqrt{1-(u'/c)^2}};$$

and this result is entirely independent of the constant velocity v with which the platform S' is moving through the æther.

This is one of the characteristic propositions of the Theory of Relativity.

Experiments with a portable clock : second physical assumption involved in the Theory of Relativity.

29. Finally, we suppose that the observers on S' have acquired a portable clock P , which they can "send by express" from one station A to another station B ; and we inquire whether the use of this portable clock will enable the observers to detect the motion of their platform S' through the æther.

30. DEFINITION. The *absolute* rate of a clock is its "observed rate" (§ 10) taken with respect to a platform S which is at rest in the æther.

Now there are two assumptions which we can make in regard to the behaviour of clocks in motion through the æther.

If we assume that the *absolute rate of a clock is not altered by transportation through the æther*, then a clock P which agreed with clock A at the beginning of its journey from A to B will continue to agree absolutely with clock A, and hence, by Theorem 3, will *not* agree with the clock at B unless the platform is at rest in the æther. Therefore by this experiment the observers could detect the motion of the platform through the æther, by noting the disagreement between the transported clock and the clock at B.

31. If, on the other hand, we make the following assumption concerning the rate of a moving clock, then this possibility will be removed, and the Principle of Relativity will again be satisfied :

ASSUMPTION B. *The "absolute rate" of a clock which is moving through the æther with a constant velocity v is less than the absolute rate of the same clock when at rest, in the ratio*

$$\frac{1}{\sqrt{1-(v/c)^2}}.$$

32. If this assumption is true, we have the following theorem, in which S' is any platform moving with constant velocity through the æther, and on which a system of coordinates has been laid out by the method of light-signals :

THEOREM 9. *If assumption B is true, the "observed rate" of a clock which is moving over a platform S' with observed velocity u' is less than the observed rate of the same clock when at rest with respect to that platform—the ratio of the rates being*

$$\frac{1}{\sqrt{1-(u'/c)^2}};$$

and this result is entirely independent of the constant velocity v with which the platform is moving through the æther.

This theorem 9 is another characteristic proposition of the Theory of Relativity.

33. It should be noticed that Assumptions A and B are not required for the proof of the transformation equations in Theorem 1; they are required only if we wish to preserve the Principle of Relativity—that is, if we wish to make it impossible for the observers on our system S' to detect their

motion through the æther ; and any experimental evidence which may be obtained for the truth of the Principle of Relativity (or for the truth of Theorems 8 and 9) may be accepted as indirect evidence for the truth of Assumptions A and B.

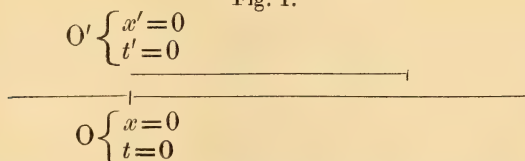
APPENDIX.

In this appendix we give an elementary method for obtaining the transformation equations of Theorem 1. As already stated, the correctness of Theorem 1 may be readily verified when once the transformation equations have been written down. The question naturally arises, however: How could anyone hit upon these equations in the first place? The purpose of this appendix is to answer this question.

We consider four positions of the moving platform S' , namely: (1) when O' is opposite O ; (2) when a light-signal starts from O' toward any station A' ; (3) when this signal arrives at A' and is immediately started back toward O' ; and (4) when the return signal has arrived at O' . We shall suppose for simplicity that A' lies on the axis $O'X'$, since the extension to the general case presents no new difficulty and may well be left to the reader; and we let the abscissa of A' , as determined by the method of light-signals, be x' .

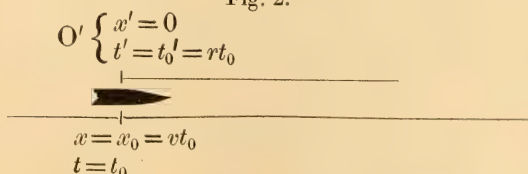
In position 1, as shown in fig. 1, the clocks at O and O' both read zero.

Fig. 1.



In position 2, at the instant when the signal starts from O' , let the clock at O' read t'_0 , and let the station which happens to be opposite O' at that instant have an abscissa x_0 and a clock-reading t_0 . Then, since the observed rate of the

Fig. 2.

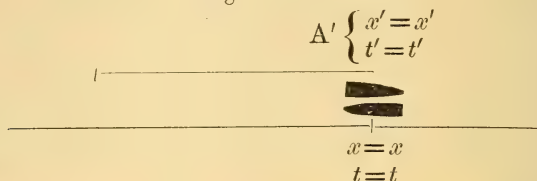


clock at O' (see § 10) is r , we must have $t'_0 = \tau t_0$. Also,

since the observed velocity of O' (see § 9) is v , we must have $x_0 = vt_0$. Hence the situation at this instant is represented by fig. 2.

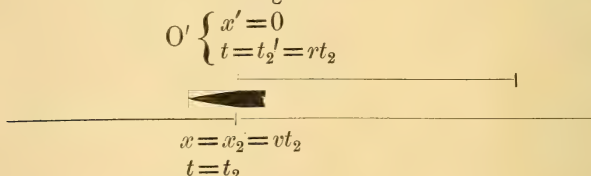
In position 3, at the instant when the signal has reached A' , let the clock at A' read t' , and let the station opposite A' at that instant have the abscissa x and the clock-reading t , as shown in fig. 3.

Fig. 3.



In position 4, at the instant when the return signal has reached O' , let the clock at O' read t'_2 , and let x_2 and t_2 be the abscissa and clock-reading of the station opposite O' at that instant. Then $t'_2 = rt_2$, since the observed rate (§ 10) of the

Fig. 4.



clock at O' in passing from position 1 to position 4 is r . Also, $x_2 = vt_2$, since the observed velocity of O' (§ 9) in passing from position 1 to position 4 is v . Hence the situation at this instant is as represented in fig. 4.

Now in the interval between fig. 2 and fig. 3, we note that a light-signal has passed along the *stationary* platform S from $x = vt_0$ to $x = x$, with velocity c ; hence, by the definition of observed velocity (§ 9),

$$\frac{x - vt_0}{t - t_0} = c. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Similarly, in the interval between fig. 3 and fig. 4, the return signal has passed from $x = x$ to $x = vt_2$ with velocity $-c$; hence,

$$\frac{vt_2 - x}{t_2 - t} = -c. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Further, from the way in which the clock at A' has been

“synchronized” with the clock at O' (see § 4), we have (from figs. 2, 3, and 4) :

$$t' = \frac{1}{2}(rt_0 + rt_2). \quad (3)$$

Finally, from the way in which the abscissa of A' has been determined (see § 5), we have (from figs. 2 and 3) :

$$x' = c(t' - rt_0). \quad (4)$$

From these four equations, the required values of x' and t' in terms of x and t are at once obtainable. Thus, solving (1) for t_0 and (2) for t_2 , and substituting in (3), we have

$$t' = \frac{r}{1 - (v/c)^2} \left(t - \frac{v}{c^2} x \right);$$

and then substituting this value, together with the value of t_0 , in (4), we have

$$x' = \frac{r}{1 - (v/c)^2} (x - vt).$$

These are the required transformation equations (§ 13), for a point A' on the axis $O'X'$. For a point A' not on the axis, a similar chain of reasoning will give

$$y' = \frac{r}{\sqrt{1 - (v/c)^2}} y,$$

as required, while the values of x' and y' remain as before.

Thus all the transformation equations used in Theorem 1 are obtained by this entirely natural and elementary method.

XLVII. The Emission and Absorption of Radiation in any Material System and Complete Radiation. By S. B. McLAREN, M.A., Assistant Lecturer in Mathematics in the University of Birmingham*.

	Page
§ 1. Results and Introduction	513
§ 2. The Definition of Radiation	516
§ 3. The Modified Lagrangian Function	520
§ 4. Expansion in Normal Functions	523
§ 5. The Perturbations due to Radiation	524
§ 6. The Absorption of Radiation	527
§ 7. The Emission and Complete Radiation	531
§ 8. Absorption and Refraction of a Simple Harmonic Wave-Train	533
§ 9. Radiation and Mechanics	536
Conclusion	542

§1. RESULTS AND INTRODUCTION.

COMPLETE or “black-body” radiation is the result of an equipoise in the radiation absorbed and that emitted by a material system. In this paper it is first shown how

* Communicated by the Author.

energy of radiation is to be distinguished from the energy which belongs to matter. For in the electromagnetic theory the material energy too is localized in the "æther" and the distinction to be made is practical and approximate, not absolute and uniquely definable. I have assumed that the electric charges constituting the material system move with velocities much smaller than the velocity of light or move in a steady distribution. Complete radiation is then shown to involve the interaction of two dynamical systems—the material system on the one side, and the field of radiation on the other.

For the motion of such material systems as are defined by Hamilton's equations

$$\frac{dq_r}{dt} = \frac{dH}{dp_r}, \quad \frac{dp_r}{dt} = -\frac{dH}{dq_r} \quad . \quad . \quad . \quad (1)$$

$(r=1, 2 \dots n)$; H is the total energy.

(1) it is to be noticed refers to the motion such as it would be if undisturbed by the radiation. $q_1 q_2 \dots q_n$ are coordinates defining the distribution. $p_1 p_2 \dots p_n$ are the momenta.

Write

$$dV_{2n} = dq_1 dq_2 \dots dq_n dp_1 dp_2 \dots dp_n \quad . \quad . \quad . \quad (2)$$

Let the probability of a distribution in which the coordinates and momenta lie in the $2n$ 'ple volume element dV_{2n} be

$$f dV_{2n} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

And let the energy of complete radiation per unit volume whose wave-length lies between λ and $\lambda + d\lambda$ be

$$E_\lambda d\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

It is shown in this paper that

$$\begin{aligned} E_\lambda \iint^{2n} (f, \phi_t) \int_0^\epsilon \phi(t-\epsilon) \sin\left(\frac{2\pi c}{\lambda} \epsilon\right) d\epsilon dV_{2n} \\ = -16\pi^2 c \lambda^{-5} \iint^{2n} f \phi_t \int_0^\epsilon \phi(t-\epsilon) \cos\left(\frac{2\pi c}{\lambda} \epsilon\right) d\epsilon dV_{2n}; \quad . \quad (5) \end{aligned}$$

$$(f, \phi_t) = \sum_{r=1}^{r=n} \left(\frac{df}{dq_r} \frac{d\phi_t}{dp_r} - \frac{df}{dp_r} \frac{d\phi_t}{dq_r} \right), \quad . \quad . \quad . \quad (6)$$

the Poisson-bracket expression. ϕ_t is a linear function of

the velocities $\frac{dq_r}{dt}$, &c., and also depends upon the coordinates g_r , &c. ϵ is a time taken large enough to ensure that all elements in the integral with respect to ϵ are included which are coordinated with ϕ_t . The average values of the functions at time t are of course to be taken on both sides of (5).

If f is a function of H only say $f(H)$ then (5) reduces to

$$E_\lambda \iint_{2n} \frac{df}{dH} \phi(t) \int_0^\epsilon \phi(t-\epsilon) \cos\left(\frac{2\pi c}{\lambda} \epsilon\right) d\epsilon dV_{2n} \\ = -8\pi\lambda^{-4} \iint_{2n} f \phi_t \int_0^\epsilon \phi(t-\epsilon) \cos\left(\frac{2\pi c}{\lambda} \epsilon\right) d\epsilon dV_{2n}. \quad (7)$$

And if f varies as $e^{-\frac{H}{R\theta}}$ as kinetic theory requires

$$E_\lambda = 8\pi R\theta\lambda^{-4}. \quad (8)$$

The method by which (5) is reached does not give that direct information as to the behaviour of a simple wave-train which is required if the results reached are to be tested by their accord with experimental evidence. I show that a plane wave can advance in any medium with the electric intensity in the wave-front. Let the electric intensity E be given by

$$E = (E_1, E_2, 0) e^{ipt - inz - kz}.$$

So that the wave advances in the direction of the axis of z . Then

$$E_1 \left(k^2 - n^2 + 2ikn + \frac{p^2}{c^2} \right) + \Phi_{11}E_1 + \Phi_{12}E_2 = 0 \quad (9)$$

$$E_2 \left(k^2 - n^2 + 2ikn + \frac{p^2}{c^2} \right) + \Phi_{21}E_1 + \Phi_{22}E_2 = 0. \quad (10)$$

And the functions Φ_{11} , Φ_{12} , Φ_{21} , Φ_{22} are determinate in terms of f and the wave-length. They are of form similar to that which stands on the left of (5). Where there is no rotation of the plane of polarization

$$\Phi_{(12)} = \Phi_{(21)} = 0.$$

From (9) and (10) the refractive index and the coefficient of absorption are determinate when the distribution f is known.

The method used throughout is to treat the radiation as a small perturbing influence in the motion of the material system. This is made possible by the absorption into that system of the whole intermolecular field which arises from charge in the immediate neighbourhood of any point.

I argue finally that the problem of the distribution of energy reduced as it is to the determination of the function f is beyond dynamics in its present state. Equipartition is a necessary inference if we assume Hamilton's equations deduced as they are from the principle of least action, and an essentially positive energy function. If we are willing to resign the law of minimum action, equations of motion differing from Hamilton's will lead to different results. Equipartition can then be avoided. But the problem of radiation is not thus brought nearer a solution. No continuous laws of motion in which energy is conserved can account for that distribution of energy which we find realized in nature. (See, however, conclusion.) Some such revolution of our physical ideas as is foreshadowed in the work of Planck and Einstein is, it would seem, inevitable; at the most it may be hoped that the future will adapt and not destroy the work of the past. In this paper "æther" still retains its classical traditional value, it is the æther of Maxwell's equations. I have determined how it would interact with matter in any continuous motion. It is only by pushing the mechanical theory to its limits that we can discover where these limits lie. But to maintain such types of motion as in reality exist, other forces must be involved than those known to our present dynamics. Only the æther then, only what is not matter is completely mechanical. Nor need this be surprising. The problem of radiation involves the ultimate constitution of matter, and the latest work on Physics makes it even more evident how inadequate mechanical ideas are to unravel that. The spectroscope shows us matter classified in distinct species without continuous change from one species to another. On any purely mechanical theory this is almost impossible to explain. If any one type of motion is possible in a dynamical system there must be others continuous with the first. And the theory of relativity removes even the possibility of rigid bodies. Where all substance is mobile how does each atom or molecule remain within such narrow limits constant to its own type? The conclusion forces itself that the mechanics which describes the motion of matter in bulk cannot deal with its ultimate parts.

§2. THE DEFINITION OF RADIATION.

Electromagnetic theory explains the inertia of matter in terms of its own fundamental concepts of electric and magnetic intensity. Thus regarded the kinetic energy of an electron is energy of the field surrounding it. In any

theory of radiation therefore it is implied, though not always explicit, that the radiation does not exhaust the whole electromagnetic field, part is always attached to the electric charge in the immediate neighbourhood. The distinction is here made precise and expressed in formulæ through which the interaction of matter and radiation can be studied. In a previous paper (Phil. Mag., January 1911) I made no attempt to distinguish in the whole field that part which is properly associated with the moving electrons. It was there shown that the complete system of matter and "æther" forms a Lagrangian dynamical system having an infinity of degrees of freedom. But the only term associated with the material part which appears in the energy is merely potential and due to the electrostatic field. Kinetic energy there is none unless it arises outside the pale of electromagnetics. Without some such source of energy the Lagrangian system cannot be reduced to Hamilton's form and the ordinary statistical methods cannot be applied. Even granted its existence, it would be unsafe to assume that taken in isolation, the purely material energy has the character of that known to us. Our experience cannot separate it as our mathematics do. The theory I give in this paper avoids the difficulty, it does not so divide where nature has joined together. But on the other hand, there is set up the new distinction between electromagnetic energy credited to the account of the material system and the energy of radiation. This too is an arbitrary distinction however great its practical importance. The price paid for insisting upon it is that our formulæ no longer represent the action of a single dynamical system. Instead there appear to be two such systems each disturbed by external forces due to the other. And when a charge moves with translational velocity comparable to that of light it does not interact dynamically with other charges, the æther in fact intervenes between them. The methods used in this paper assume therefore that the square of the velocity of a charge divided by the square of the velocity of light is negligible.

The equations of the electromagnetic field are

$$\left(\nabla^2 - \frac{1}{c^2} \frac{d^2}{dt^2}\right) \mathbf{F} + 4\pi\rho \frac{\mathbf{u}}{c} = 0 \quad . \quad . \quad . \quad (11)$$

$$\left(\nabla^2 - \frac{1}{c^2} \frac{d^2}{dt^2}\right) \phi + 4\pi\rho = 0 \quad . \quad . \quad . \quad . \quad (12)$$

$$\frac{1}{c} \frac{d\phi}{dt} + \text{Div } \mathbf{F} = 0 \quad . \quad . \quad . \quad . \quad (13)$$

$\mathbf{F}$ and ϕ are the vector and scalar potential, $\mathbf{u}$ the vector velocity of the charge whose density is ρ at any point. Regarding (13) as a condition imposed upon $\mathbf{F}$ and ϕ (11) and (12) can be deduced by making the variation of the action zero.

$$\delta \iiint L dv dt = 0. \quad . \quad . \quad . \quad (14)$$

$$L = \frac{1}{8\pi} \left(\frac{1}{c} \frac{d\mathbf{F}}{dt} + \nabla \phi \right)^2 - \frac{1}{8\pi} (\text{Curl } \mathbf{F})^2 + \rho \left(\frac{\mathbf{u}\mathbf{F}}{c} - \phi \right) + L_m. \quad (15)$$

In (14) dv is any element of volume in the field. L_m in case it exists is the Lagrangian function of material origin. It may be shown that the principle of relativity allows L_m to be any function of $\rho^2(1 - \mathbf{u}^2/c^2)$ but this is not used in what follows (L is invariant under a Lorentz-Einstein substitution). The equations of motion of the electric charge can be inferred from (15) combined with the equation of continuity

$$\frac{d\rho}{dt} + \text{Div. } \rho\mathbf{u} = 0. \quad . \quad . \quad . \quad (16)$$

$$\text{Write} \quad \mathbf{F} = \mathbf{F}_1 + \mathbf{F}_0 + \nabla \chi, \quad . \quad . \quad . \quad (17)$$

$$\text{where} \quad \text{Div. } \mathbf{F}_1 = 0 \quad . \quad . \quad . \quad (18)$$

$$\text{Div. } \mathbf{F}_0 = 0 \quad . \quad . \quad . \quad (19)$$

χ and $\mathbf{F}_0$ will be so chosen as to make (18) and (19) possible. (17) gives

$$\nabla^2 \chi = \text{Div. } \mathbf{F} = -\frac{1}{c} \frac{d\phi}{dt} \text{ by (13), (18), (19), } . \quad . \quad (20)$$

$$\nabla \left(\frac{1}{c} \frac{d\chi}{dt} + \phi \right) = \left(\nabla^2 - \frac{1}{c^2} \frac{d^2}{dt^2} \right) \phi = -4\pi\rho \text{ by (12).}$$

$$\text{Hence if} \quad \frac{1}{c} \frac{d\chi}{dt} + \phi = \phi_0, \quad . \quad . \quad . \quad (21)$$

$$\text{then} \quad \nabla^2 \phi_0 + 4\pi\rho = 0. \quad . \quad . \quad . \quad (22)$$

So that ϕ_0 is the potential of the charge ρ . I suppose the volume V containing the radiation to be bounded by a surface S as far distant from the radiating matter as we please. ϕ_0 is to be so chosen as to vanish at S , which will be supposed perfectly conducting.

From (20)

$$\left(\nabla^2 - \frac{1}{c^2} \frac{d^2}{dt^2} \right) \chi = -\frac{1}{c} \frac{d}{dt} \left(\frac{1}{c} \frac{d\chi}{dt} + \phi \right) = -\frac{1}{c} \frac{d\phi_0}{dt} \quad . \quad (23)$$

I define F_0 as that solution of the equation

$$(\nabla^2 - \kappa^2)F_0 + 4\pi \frac{\rho \mathbf{u}}{c} = \nabla \left(\frac{1}{c} \frac{d\phi_0}{dt} \right) \quad . \quad . \quad (24)$$

which is normal at the surface S. κ^{-1} is a length large compared with the radius of action of the intermolecular forces but small in comparison with the wave-length of the radiation involved. The phenomena of gases show that neighbouring molecules do not affect each other sensibly till the distance between their centres is of the order 10^{-8} ; it would be sufficient we shall find to take κ^{-1} equal to 10^{-6} or even 10^{-7} .

$$F_0 = \iiint \frac{e^{-\kappa r}}{cr} \left(\rho \mathbf{u} - \frac{1}{4\pi} \nabla \frac{d\phi_0}{dt} \right) dv. \quad . \quad . \quad (25)$$

Thus the value of F_0 given by (25) at any point is contributed entirely by elements of volume dv which are within distances of the point small compared with the wave-length.

Substitute from (17) in (11)

$$\left(\nabla^2 - \frac{1}{c^2} \frac{d^2}{dt^2} \right) (F_1 + F_0) + 4\pi \frac{\rho \mathbf{u}}{c} = \nabla \left(\frac{1}{c} \frac{d\phi_0}{dt} \right) \quad . \quad (26)$$

$$F_1 + F_0 = \iiint \frac{1}{cr} \left(\rho \mathbf{u} - \frac{1}{4\pi} \nabla \frac{d\phi_0}{dt} \right) dr. \quad . \quad . \quad (27)$$

$t - \frac{r}{c}$

Now the elements of the integrals in (25) and (27) are identical so long as $e^{-\kappa r} = 1$

and
$$\left(\rho \mathbf{u} - \frac{1}{4\pi} \nabla \frac{d\phi_0}{dt} \right)_t = \left(\rho \mathbf{u} - \frac{1}{4\pi} \nabla \frac{d\phi_0}{dt} \right)_{t - \frac{r}{c}}.$$

The first condition means that r is to be small compared with κ^{-1} . The second that the distribution and velocity of the charge within the molecular radius r are not to alter appreciably during the time it takes light to travel that distance. This is of course ensured in any steady distribution of electric currents. It also holds if the velocity $\mathbf{u}$ is small compared with the velocity of light, and if the rate of change of $\mathbf{u}$ is such that the radiation emitted is of wave-length large compared with the distance r . Under these conditions (25) and (27) show that all that part of $F_1 + F_0$ which arises from the charge within the molecular radius is included in F_0 . Thus the inter-atomic forces are removed from F_1 , and it represents the radiation proper, a force producing only a small disturbance in the motion of the material system*.

* See Phil. Mag. July 1911, p. 69.

§3. THE MODIFIED LAGRANGIAN FUNCTION.

The equations of motion can be deduced from a modified Lagrangian Function derived by substituting the value of F given by (17). From (26) and (24) we have directly

$$\left(\nabla^2 - \frac{1}{c^2} \frac{d^2}{dt^2}\right) F_1 = \frac{1}{c^2} \frac{d^2}{dt^2} F_0 - \kappa^2 F_0. \quad (28)$$

The variation of F and ϕ in (14) leads to (11) and (12) which are now replaced by (28). Varying ρ and u

$$\delta \int_4 L_m dv dt + \int_4 \left(F \delta \frac{\rho u}{c} - \phi \delta \rho \right) dv dt = 0 \quad (29)$$

Use (17)

$$\begin{aligned} \delta \int_4 L_m dv dt + \int_4 \left\{ (F_0 + \nabla \chi) \delta \frac{\rho u}{c} - \phi \delta \rho \right\} dv dt \\ = - \int_4 F_1 \delta \frac{\rho u}{c} dv dt \quad (30) \end{aligned}$$

The action may always be modified by omitting any term which is merely a perfect differential

$$\int_4 \nabla \chi \delta \frac{\rho u}{c} dv dt = \int_4 \chi \frac{1}{c} \frac{d}{dt} (\delta \rho) dv dt = - \int_4 \delta \rho \frac{1}{c} \frac{d\chi}{dt} dv dt.$$

And (30) becomes

$$\delta \int_4 L_m dv dt + \int_4 \left(F_0 \delta \frac{\rho u}{c} - \phi_0 \delta \rho \right) dv dt = - \int_4 F_1 \delta \frac{\rho u}{c} dv dt. \quad (31)$$

By (24)

$$(\nabla^2 - \kappa^2) \delta F_0 + 4\pi \delta \frac{\rho u}{c} = \nabla \left(\delta \frac{1}{c} \frac{d\phi_0}{dt} \right) \quad (32)$$

So that

$$\begin{aligned} F_0 (\nabla^2 - \kappa^2) \delta F_0 - \delta F_0 (\nabla^2 - \kappa^2) F_0 + 4\pi \left(F_0 \delta \frac{\rho u}{c} - \frac{\rho u}{c} \delta F_0 \right) \\ = F_0 \nabla_m \left(\delta \frac{1}{c} \frac{d\phi_0}{dt} \right) - \delta F_0 \nabla \frac{1}{c} \left(\frac{d\phi_0}{dt} \right). \quad (33) \end{aligned}$$

Now the function F_0 as defined by (24) is such that

$$\text{Div } F_0 = 0 \text{ and } F_0 \text{ normal at } S.$$

Thus we have also

$$\text{Div } \delta F_0 = 0 \text{ and } \delta F_0 \text{ normal at } S.$$

These conditions can be imposed on δF_0 because F_0 is defined by (24) completely as a function of the distribution and velocity of the charge.

Now at any surface where F_0 is normal the condition $\text{Div } F_0 = 0$ reduces to

$$\frac{dF_0}{d\nu} + \left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right)F_0 = 0. \quad (34)$$

where $\frac{d}{d\nu}$ denotes differentiation along the outward drawn normal ν and ρ_1, ρ_2 are the principal radii of curvature. (34) and the similar result for δF_0 gives

$$\delta F_0 \frac{d}{d\nu} F_0 - F_0 \frac{d}{d\nu} \delta F_0 = 0. \quad (35)$$

Multiply (33) by $d\nu$ and integrate throughout the volume V

$$\begin{aligned} \int_2 \left(F_0 \frac{d}{d\nu} \delta F_0 - \delta F_0 \frac{d}{d\nu} F_0 \right) dS + 4\pi \int_3 \left(F_0 \delta \frac{\rho_{11}}{c} - \delta F_0 \frac{\rho_{11}}{c} \right) dv \\ = \int_3 F_0 \nabla \left(\delta \frac{1}{c} \frac{d\phi_0}{dt} \right) dv - \int_3 \delta F_0 \nabla \left(\frac{1}{c} \frac{d\phi_0}{dt} \right) dv. \end{aligned}$$

Use (35) and notice that the right-hand side vanishes by partial integration since ϕ_0 is zero at S . We have

$$\int_3 \left(F_0 \delta \frac{\rho_{11}}{c} - \delta F_0 \frac{\rho_{11}}{c} \right) dv = 0,$$

or

$$\int_3 F_0 \delta \frac{\rho_{11}}{c} dv = \frac{1}{2} \delta \int_3 F_0 \frac{\rho_{11}}{c} dv,$$

also

$$\int_3 \phi_0 \delta \rho dv = \frac{1}{2} \delta \int_3 \phi_0 \rho dv.$$

(31) reduces to

$$\delta \int L_m' dt = - \int_4 F_1 \delta \frac{\rho_{11}}{c} dv dt, \quad (36)$$

where

$$L_m' = \int_3 \left\{ L_m + \frac{1}{2} \rho \left(\frac{11 F_0}{c} - \phi_0 \right) \right\} dv. \quad (37)$$

Or (36) may be written

$$\delta \int L_m' dt + \delta \int F_1 \frac{\rho u}{c} dv dt = 0 \quad . \quad . \quad . \quad (38)$$

Where it is understood that F_1 given as a function of the time and the coordinates of any point of the field is not to be varied, but only the distribution and movement of charge.

Write
$$\int F_1 \frac{\rho u}{c} dv = \Phi. \quad . \quad . \quad . \quad . \quad . \quad (39)$$

Then (36) gives the equations of motion

$$\frac{d}{dt} \left(\frac{dL_m'}{du_r} \right) - \frac{dL_m}{dq_r} = + \frac{d\Phi}{dq_r} - \frac{d}{dt} \left(\frac{d\Phi}{du_r} \right) \quad . \quad . \quad . \quad (40)$$

The coordinates defining the position of the charge being

$$q_1, q_2, q_r \dots q_n. \quad (r=1, 2, \dots n),$$

and
$$u_r = \frac{dq_r}{dt}$$

If we transform to Hamilton's form

$$\left. \begin{aligned} H = \sum_r u_r \frac{dL_m'}{du_r} - L_m' \\ \frac{dp_r}{dt} - \frac{dH}{dq_r} = \frac{d\Phi}{dq_r} - \frac{d}{dt} \left(\frac{d\Phi}{du_r} \right), \quad \frac{dq_r}{dt} + \frac{dH}{dp_r} = 0 \end{aligned} \right\} \quad (r=1, 2 \dots n) \quad (41)$$

And (41) is true whatever may be the nature of the coordinates.

If we hold an atomic theory of matter n will be finite. If, on the other hand, charge is continuously distributed there will be an infinity of degrees of freedom. The only method then available is to start from a configuration of equilibrium or steady motion and to study the vibrations about that as the mean position.

The theory of emission and absorption which follows applies in either case. But I am not able to cope with the transition from one state of steady motion to another involving a new system of vibrations. For in such a process the degrees of freedom are no longer enumerable. It may be that a radio-active transformation is an instance. Before the change and after it we have an enumerable infinity of degrees of freedom. There intervenes an action by which one set of degrees of freedom disappears and the other is

substituted. So regarded the change is beyond the pale of dynamical actions. Of course it may be urged that the point of view is not ultimate. What is before us is really a dynamical process. I have argued that this may be doubted. In practice at all events we are forced in the present state of our knowledge or ignorance to deal only with the enumerable infinite.

§ 4. EXPANSION IN NORMAL FUNCTIONS.

The value of F_1 satisfying (28) is to be normal at S. Write therefore

$$F_1 = \sum_{m=1}^{m=\infty} \alpha_m F_m, \quad . \quad . \quad . \quad . \quad . \quad (42)$$

where

$$\left. \begin{aligned} (\nabla^2 + \kappa_m^2) F_m &= 0 \\ \text{Div } F_m &= 0 \\ \int_3 F_m^2 dv &= 4\pi \\ F_m \text{ normal at S} \\ \int_3 F_m F_{m_1} dv &= 0 \end{aligned} \right\} . \quad . \quad . \quad . \quad . \quad (43)$$

The last of (43) is the normal property holding for any two different values of m , it follows from the others. Where V is large these normal functions became ordinary trigonometrical functions and $2\pi\kappa_m^{-1}$ is the wave-length corresponding to F_m .

As in (34) and (35) at S

$$F_1 \frac{d}{dv} F_m - F_m \frac{d}{dv} F_1 = 0.$$

So that

$$\int_3 F_m \nabla^2 F_1 dv = \int_3 F_1 \nabla^2 F_m dv = -\kappa_m^2 \int_3 F_1 F_m dv. \quad . \quad (44)$$

Also

$$\int_3 F_1 F_m dv = 4\pi \alpha_m. \quad . \quad . \quad . \quad . \quad (45)$$

Multiply (24) throughout by $F_m dv$ and integrate

$$\int_3 F_m (\nabla^2 - \kappa^2) F_0 dv + 4\pi \int_3^{\rho u} F_m dv = \int F_m \nabla \left(\frac{1}{c} \frac{d\phi_0}{dt} \right) dv.$$

Now

$$\int F_m \nabla^2 F_0 dv = -\kappa_m^2 \int_3 F_0 F_m dv,$$

as in (44),

$$\int_3 F_m \nabla \left(\frac{1}{c} \frac{d\phi_0}{dt} \right) dv = 0$$

since ϕ_0 is zero at S. Hence the above equation reduces to

$$(\kappa^2 + \kappa_m^2) \int_3 F_0 F_m dv = 4\pi \int_3 \frac{\rho_1}{c} F_m dv.$$

Multiply (28) throughout by $F_m dv$ and integrate, using (44) and (45). Then

$$\frac{1}{c^2} \frac{d^2 \alpha_m}{dt^2} + \kappa_m^2 \alpha_m = \frac{\kappa^2}{4\pi} \int F_0 F_m dv - \frac{1}{4\pi c^2} \frac{d^2}{dt^2} \int F_0 F_m dv.$$

Write
$$\phi_m = \int \frac{\rho_1}{c} F_m dv \quad . \quad . \quad . \quad . \quad . \quad (46)$$

Then

$$\frac{1}{c^2} \frac{d^2 \alpha_m}{dt^2} + \kappa_m^2 \alpha_m = \frac{1}{\kappa^2 + \kappa_m^2} \left(\kappa^2 \phi_m - \frac{1}{c^2} \frac{d^2 \phi_m}{dt^2} \right). \quad . \quad (47)$$

And in (39)

$$\Phi = \sum_{m=0}^{m=\infty} \alpha_m \phi_m \quad . \quad . \quad . \quad . \quad . \quad (48)$$

The equations (41) and (47) represent completely the interactions of the field of radiation and the material system.

§5. THE PERTURBED MOTION.

The course followed by the material system is slightly disturbed by the field of radiation represented by the terms in Φ in (41). Hence there is absorption of the radiant energy. The deviation produced in the immediate past alone causes the absorption at any instant. In the simple theory of metallic conduction it is the deviation arising within the time of a free path. The collision which preceded that free path has wiped out all that went before. Whatever the character of the dynamical system it is evident that the intramolecular forces determine the path it follows, and that the deviation which is connected with the absorption at time t is that which has been produced within some very small interval of time ϵ preceding.

Let $c_1 c_2 \dots c_{2n}$ be $2n$ constants representing coordinates and momenta at any time in the undisturbed motion. Let δp_r and δq_r be the deviations in the values of p_r and q_r at

time t due to the radiation. Then by the method of variation of elements,

$$\sum_{r=1}^{r=n} \left(\delta p_r \frac{dq_r}{dc_s} - \delta q_r \frac{dp_r}{dc_s} \right) = \int \sum_{r=1}^{r=n} \frac{dq_r}{dc_s} \left\{ \frac{d\Phi}{dq_r} - \frac{d}{dt} \frac{d\Phi}{du_r} \right\} . \quad (49)$$

In (49) the lower limit is left indeterminate so that the particular values of $c_1 c_2 \dots c_n$, that is the particular undisturbed motion from which the deviation is measured, is not fixed nor is it necessary to do so.

On the right hand of (49) the values of p_r and q_r may be either these in the actual disturbed motion or in the undisturbed motion, for the terms in question are already small of the first order in Φ representing the force of radiation. Our justification for neglecting squares of the deviation is not only to be found in the actual calculation given in another paper (see Phil. Mag. July 1911), but in the undisputed fact that absorption is always proportional to the intensity of radiation.

There are $2n$ equations such as (49) in which s takes all values from 1 to $2n$.

$$\begin{aligned} \sum_{r=1}^{r=n} \frac{dq_r}{dc_s} \left\{ \frac{d\Phi}{dq_r} - \frac{d}{dt} \left(\frac{d\Phi}{du_r} \right) \right\} &= \sum_{r=1}^{r=n} \left\{ \frac{d\Phi}{dq_r} \frac{dq_r}{dc_s} + \frac{d\Phi}{du_r} \frac{du_r}{dc_s} \right\} \\ &\quad - \sum_{r=1}^{r=n} \left\{ \frac{d\Phi}{du_r} \frac{d}{dt} \left(\frac{dq_r}{dc_s} \right) + \frac{d}{dt} \left(\frac{d\Phi}{du_r} \right) \cdot \frac{dq_r}{dc_s} \right\} \\ &= \frac{d\Phi}{dc_s} - \sum_{r=1}^{r=n} \frac{d}{dt} \left(\frac{d\Phi}{du_r} \frac{dq_r}{dc_s} \right), \end{aligned}$$

since Φ is a function of the u 's and q 's and $u_r = \frac{dq_r}{dt}$, (49) then becomes

$$\sum_{r=1}^{r=n} \delta p_r \frac{dq_r}{dc_s} - \delta q_r \frac{dp_r}{dc_s} = \frac{d}{dc_s} \int^t \Phi dt - \sum_{r=1}^{r=n} \frac{d\Phi}{du_r} \frac{dq_r}{dc_s}.$$

Solving these

$$\delta p_r + \frac{d\Phi}{du_r} = \sum_{s=1}^{s=2n} M_{rs} \frac{d}{dc_s} \int^t \Phi dt \quad (50)$$

$$\delta q_r = - \sum_{s=1}^{s=2n} M'_{rs} \frac{d}{dc_s} \int^t \Phi dt \quad (51)$$

M is the minor of $\frac{dq_r}{dc_s}$ and M'_{rs} the minor of $\frac{dp_r}{dc_s}$ in the

determinant Δ below. Since the constants c 's are values of the coordinates at some time $\Delta=1$,

$$\Delta = \begin{vmatrix} \frac{dq_1}{dc_1} \frac{dp_1}{dc_1} & \frac{dq_2}{dc_1} \frac{dp_2}{dc_1} & \frac{dq_3}{dc_1} \frac{dp_3}{dc_1} & \dots \\ \frac{dq_1}{dc_2} \frac{dp_1}{dc_2} & \dots & \dots & \dots \\ \frac{dq_1}{dc_3} \frac{dp_1}{dc_3} & \dots & \dots & \dots \end{vmatrix}$$

There are $2n$ rows and columns.

From the form of Δ it follows

$$\sum_{s=1}^{s=2n} \frac{d}{dc_s} M_{rs} = 0. \quad . \quad . \quad . \quad . \quad (52)$$

$$\sum_{s=1}^{s=2n} \frac{d}{dc_s} M'_{rs} = 0 \quad . \quad . \quad . \quad . \quad (53)$$

And (50) and (51) become

$$\delta p_r + \frac{d\Phi}{du_r} = \sum_{s=1}^{s=2n} \frac{d}{dc_s} \left(M_{rs} \int^t \Phi dt \right) \quad . \quad . \quad . \quad . \quad (54)$$

$$\delta q_r = - \sum_{s=1}^{s=2n} \frac{d}{dc_s} \left(M'_{rs} \int^t \Phi dt \right) \quad . \quad . \quad . \quad . \quad (55)$$

Consider any function ψ of the p 's and q 's which may also contain the time explicitly. The increment in value $\delta\psi$ of this function above that which it would have had in the undisturbed motion is given by

$$\begin{aligned} \delta\psi &= \sum_{r=1}^{r=n} \left(\frac{d\psi}{dp_r} \delta p_r + \frac{d\psi}{dq_r} \delta q_r \right), \\ \delta\psi &= - \sum_{r=1}^{r=n} \frac{d\psi}{dp_r} \frac{d\Phi}{du_r} + \sum_{r=1}^{r=n} \sum_{s=1}^{s=2n} \left\{ \frac{d\psi}{dp_r} \frac{d}{dc_s} \left(M_{rs} \int^t \Phi dt \right) - \frac{d\psi}{dq_r} \frac{d}{dc_s} \left(M'_{rs} \int^t \Phi dt \right) \right\} \\ &= - \sum_{r=1}^{r=n} \frac{d\psi}{dp_r} \frac{d\Phi}{du_r} + \sum_{r=1}^{r=n} \sum_{s=1}^{s=2n} \frac{d}{dc_s} \left\{ \left(M_{rs} \frac{d\psi}{dp_r} - M'_{rs} \frac{d\psi}{dq_r} \right) \int^t \Phi dt \right\} \\ &\quad - \sum_{r=1}^{r=n} \sum_{s=1}^{s=2n} \left\{ M_{rs} \frac{d}{dc_s} \left(\frac{d\psi}{dp_r} \right) - M'_{rs} \frac{d}{dc_s} \left(\frac{d\psi}{dq_r} \right) \right\} \int^t \Phi dt. \quad (56) \end{aligned}$$

If χ be any function whatever of the p 's and q 's

$$\frac{d\chi}{dc_s} = \sum_{r=1}^{r=n} \left(\frac{d\chi}{dq_r} \frac{dq_r}{dc_s} + \frac{d\chi}{dp_r} \frac{dp_r}{dc_s} \right) (s=1, 2 \dots 2n).$$

And on solving these equations

$$\sum_{s=1}^{s=2n} M_{rs} \frac{d\chi}{dc_s} = \frac{d\chi}{dq_r} \quad . \quad . \quad . \quad . \quad (57)$$

$$\sum_{s=1}^{s=2n} M'_{rs} \frac{d\chi}{dc_s} = \frac{d\chi}{dp_r} \quad . \quad . \quad . \quad . \quad (58)$$

Putting $\chi = \frac{d\psi}{dp}$ (57) gives

$$\sum_{s=1}^{s=2n} M_{rs} \frac{d}{dc_s} \left(\frac{d\psi}{dp_r} \right) = \frac{d^2\psi}{dq_r dp_r},$$

and putting $\chi = \frac{d\psi}{dq_r}$ (58) gives also

$$\sum_{s=1}^{s=2n} M'_{rs} \frac{d}{dc_s} \left(\frac{d\psi}{dq_r} \right) = \frac{d^2\psi}{dp_r dq_r}.$$

Then the last term in (56) disappears and

$$\delta\psi = - \sum_{r=1}^{r=n} \frac{d\psi}{dp_r} \frac{d\Phi}{du_r} + \sum_{r=1}^{r=n} \sum_{s=1}^{s=2n} \frac{d}{dc_s} \left\{ \left(M_{rs} \frac{d\psi}{dp_r} - M'_{rs} \frac{d\psi}{dq_r} \right) \int^t \Phi dt \right\} \quad . \quad . \quad . \quad . \quad (59)$$

§6. THE ABSORPTION OF RADIATION.

In order to arrive at the nature of complete radiation I suppose the radiating material system enclosed in a very much larger volume of space devoid of matter. The boundary surface S is at a great distance. The nature of complete radiation is of course unaffected but the formula (47) is greatly simplified. Since F_r satisfies the equation

$$\int F_m^2 dV = 4\pi,$$

it appears that the average value of F_m decreases inversely as $V^{\frac{1}{2}}$. On the other hand, the average value of $\frac{1}{2c^2} \left(\frac{dx_m}{dt} \right)^2$ is the kinetic energy belonging to a single degree of freedom. On the theory of equipartition this is always equal to the average kinetic energy of an atom, in fact it is something less than this in a ratio which depends upon the wave-length $2\pi(\kappa_m)^{-1}$, but does not depend upon the volume V . Thus by

increasing V (47) becomes the equation of motion of a simple pendulum disturbed by a very small force; and for a number of oscillations which can be made as large as we please by taking V large enough the oscillations of this pendulum are simple harmonic, and gradually change their amplitude and phase. In calculating the absorption of radiation by matter we can therefore suppose α_m which occurs in Φ to be simple harmonic of period $2\pi(\kappa_m c)^{-1}$ and find the rate of absorption due to this term alone disturbing the material system. The emission of radiation is due to whatever part of ϕ_m in (47) is of the same period and it can be found by the Fourier Analysis.

The absorption of radiation is at the rate

$$-\int \frac{\rho_{11}}{c} \frac{dF_1}{dt} dv,$$

or taking only the term $\alpha_m F_m$ in F_1

$$\begin{aligned} & -\frac{d\alpha_m}{dt} \int \frac{\rho_{11}}{c} F_m dV \\ & = -\frac{d\alpha_m}{dt} \phi_m. \quad \dots \dots \dots (60) \end{aligned}$$

The absorption is due entirely to the deviation caused by the radiation and in the absence of any deviation the average value of the absorption would be zero. Instead, therefore, of (60) we may put

$$-\frac{d\alpha_m}{dt} \delta\phi_m, \quad \dots \dots \dots (61)$$

and calculate $\delta\phi_m$ by writing ϕ_m for ψ in (59). Only the term $\alpha_m \phi_m$ in the series for Φ need be retained since the others are not correlated with $\frac{d\alpha_m}{dt}$ in (61). Hence (61) reduces to

$$\alpha_m \frac{d\alpha_m}{dt} \frac{d\phi_m}{dp_r} \frac{d\phi_m}{du_r} - \frac{d\alpha_m}{dt} \sum_{r=1}^{r=n} \sum_{s=1}^{s=2n} \frac{d}{dc_s} \left\{ \left(M_{rs} \frac{d\phi_m}{dp_r} - M'_{rs} \frac{d\phi_m}{dq_r} \right) \int^t \alpha_m \phi_m dt. \right\}$$

And the first term vanishes since the average value of $\alpha_m \frac{d\alpha_m}{dt}$ is zero in a steady state. Thus putting A_m for the average rate of absorption of radiation of wave-length $2\pi(\kappa_m c)^{-1}$,

$$\begin{aligned} A_m = & -\frac{d\alpha_m}{dt} \iiint \sum_{r=1}^{r=n} \sum_{s=1}^{s=2n} \frac{d}{dc_s} \left\{ \left(M_{rs} \frac{d\phi_m}{dp_r} - M'_{rs} \frac{d\phi_m}{dq_r} \right) \int^t \alpha_m \phi_m dt \right\} dV_{2n}, \\ & \dots \dots \dots (62) \end{aligned}$$

where we assign to each configuration at time t the probability $f dV_{2n}$. Neglect as before in the calculation of (62) the differences δp_r , δq_r &c. between the actual values of p_r , q_r , and those which belong to the undisturbed motion. Then

$$\begin{aligned} dV_{2n} &= dq_1 \, dq_2 \dots dq_n, \, dp_1 \, dp \dots dp_{2n} \\ &= dc_1 \, dc_2 \dots dc_{2n}. \end{aligned}$$

And (62) can now be transformed by partial integration with respect to the c 's,

$$\begin{aligned} A_m &= \frac{d\alpha_m}{dt} \iint_{2n} \sum_{r=1}^{r=n} \sum_{s=1}^{s=2n} \left(\frac{df}{dc_s} M_{rs} \frac{d\phi_m}{dp_r} - \frac{df}{dc_s} M'_{rs} \frac{d\phi_m}{dq_r} \right) \int^t \alpha_m \phi_m \, dt' \, dV_{2n} \\ &= \frac{d\alpha_m}{dt} \iint_{2n} \sum_{r=1}^{r=n} \left(\frac{df}{dq_r} \frac{d\phi_m}{dp_r} - \frac{df}{dp_r} \frac{d\phi_m}{dq_r} \right) \int^t \alpha_m \phi_m \, dt' \, dV_{2n}. \end{aligned}$$

Using (57) and (58), or

$$A_m = \frac{d\alpha_m}{dt} \iint_{2n} (f, \phi_m) \int^t \alpha_m \phi_m \, dt' \, dV_{2n} \dots \dots \dots (63)$$

And the lower limit in the integration for t need only be chosen so as to include all elements in the integral which are coordinated with (f, ϕ_m) the Poisson-bracket expression. α_m is periodic in the time $2\pi(\kappa_m c)^{-1}$. Hence for a large number of periods write

$$\alpha_m = (\alpha_m)_0 \cos c\kappa_m t + \left(\frac{d\alpha_m}{dt} \right)_0 \frac{1}{c\kappa_m} \sin c\kappa_m t;$$

where $(\alpha_m)_0$ and $\left(\frac{d\alpha_m}{dt} \right)_0$ are the values of α_m and $\frac{d\alpha_m}{dt}$ at time $t=0$.

We require the average value of

$$\frac{d\alpha_m}{dt} \int^t \alpha_m \phi_m \, dt';$$

$$\begin{aligned} \text{it is} \quad & \frac{1}{c\kappa_m} \left(\frac{d\alpha_m}{dt} \right)_0^2 \int^t \phi_m \cos c\kappa_m t \sin c\kappa_m t' \, dt' \\ & - c\kappa_m (\alpha_m)_0^2 \int^t \phi_m \sin c\kappa_m t \cos c\kappa_m t' \\ & = - \frac{1}{c\kappa_m} \left(\frac{d\alpha_m}{dt} \right)_0^2 \int^t \phi_m \sin (c\kappa_m t - c\kappa_m t') \, dt', \\ & = - \frac{1}{c\kappa_m} \left(\frac{d\alpha_m}{dt} \right)_0^2 \int_0^t \phi_m(t-\epsilon) \sin (c\kappa_m \epsilon) \, d\epsilon. \end{aligned}$$

where I have written $t-t'=\epsilon$ and ϵ in the upper limit is to be determined as already explained. I have also assumed that on the average

$$\alpha_m \frac{d\alpha_m}{dt} = 0 \quad \text{and} \quad \left(\frac{d\alpha_m}{dt} \right)_0^2 = c^2 \kappa_m^2 \alpha_m^2.$$

(63) reduces to

$$A_m = - \frac{2c}{\kappa_m} \frac{1}{2c^2} \left(\frac{d\alpha_m}{dt} \right)_0^2 \iint_{2n} (f, \phi_m) \int_0^\epsilon \phi_m((t-\epsilon) \sin(c\kappa_m\epsilon)) d\epsilon dV_{2n} \quad (64)$$

(64) can be put in another form when the wave-length $2\pi\kappa_m^{-1}$ is very small compared with the dimensions of the enclosure, as may always be ensured by making the enclosure large enough.

$E_\lambda d\lambda$ is the total energy per unit volume of the radiation of wave-length in the interval $d\lambda$, and λ for the m 'th normal function is to be $2\pi\kappa_m^{-1}$. Then we shall have

$$V E_\lambda d\lambda = V \frac{16\pi d\lambda}{\lambda^4} \frac{1}{2c^2} \left(\frac{d\alpha_m}{dt} \right)^2 \quad . \quad . \quad . \quad (65)$$

This expresses the fact that in the interval $d\lambda$ there are $V 8\pi\lambda^{-4} d\lambda$ normal vibrations each having a total energy equal to $\frac{1}{c^2} \left(\frac{d\alpha_m}{dt} \right)^2$ which is twice the kinetic energy. (See

Rayleigh on "Complete Radiation," *Phil. Mag.* xlix. p. 540.) The result may be compared with Rayleigh's formula for the radiation of great wave-length in accordance with which

$$E_\lambda d\lambda = 8\pi R \theta \lambda^{-4} d\lambda^*.$$

Since $\frac{1}{2}R\theta$ is the kinetic energy of an atom at the temperature θ it follows that the total energy of radiation in the volume V is

$$V 16\pi\lambda^{-4} d\lambda$$

times the kinetic energy of an atom. Allowing equal kinetic and potential energies to each "æthereal" degree of freedom there must be the number

$$V 8\pi\lambda^{-4} d\lambda$$

in the interval $d\lambda$.

* The numerical factor 8π is left undetermined in Rayleigh's paper.

Writing therefore in accordance with (65)

$$\frac{1}{2c^2} \left(\frac{d\alpha_m}{dt} \right)^2 = \frac{\lambda^4}{16\pi} E_\lambda, \text{ and } \lambda = \frac{2\pi}{\kappa_m} \text{ in (64),}$$

$$A_m = -\frac{c\lambda^5}{16\pi^2} E_\lambda \int_{2n}^{\infty} (f, \phi_\lambda) \int_0^\epsilon \phi_\lambda(t-\epsilon) \sin\left(\frac{2\pi c}{\lambda} \epsilon\right) d\epsilon dV_{2n}, \quad (66)$$

writing ϕ_λ for ϕ_m .

§ 7. THE EMISSION OF RADIATION AND COMPLETE RADIATION.

The rate of emission R_m to the m 'th æthereal degree of freedom can be found by (47). Integration gives

$$\alpha_m = \frac{c}{\kappa_m(\kappa^2 + \kappa_m^2)} \int^t \left(\kappa^2 \phi_m - \frac{1}{c^2} \frac{d^2 \phi_m}{dt'^2} \right) \sin(c\kappa_m t - c\kappa_m t') dt'$$

$$\frac{d\alpha_m}{dt} = \frac{c^2}{(\kappa^2 + \kappa_m^2)} \int^t \left(\kappa^2 \phi_m - \frac{1}{c^2} \frac{d^2 \phi_m}{dt'^2} \right) \cos(c\kappa_m t - c\kappa_m t') dt',$$

or

$$\frac{d\alpha_m}{dt} = \frac{c^2}{(\kappa^2 + \kappa_m^2)} \int_0^{t-\epsilon} \left(\kappa^2 \phi_m - \frac{1}{c^2} \frac{d^2 \phi_m}{d\epsilon^2} \right) \cos(c\kappa_m \epsilon) d\epsilon.$$

And

$$R_m = \frac{c^2}{(\kappa^2 + \kappa_m^2)^2} \left(\kappa^2 \phi_m - \frac{1}{c^2} \frac{d^2 \phi_m}{dt^2} \right) \int_0^\epsilon \left(\kappa^2 \phi_m - \frac{1}{c^2} \frac{d^2 \phi_m}{d\epsilon^2} \right) \cos(c\kappa_m \epsilon) d\epsilon, \quad (69)$$

with the same significance for ϵ as before $t' = t - \epsilon$.

$$\int_0^\epsilon \frac{d^2 \phi_m}{d\epsilon^2} \cos(c\kappa_m \epsilon) d\epsilon = \left[\frac{d\phi_m}{d\epsilon} \cos c\kappa_m \epsilon \right]_0^\epsilon + c\kappa_m \int_0^\epsilon \frac{d\phi_m}{d\epsilon} \sin c\kappa_m \epsilon d\epsilon$$

$$= \left[\frac{d\phi_m}{d\epsilon} \cos c\kappa_m \epsilon + c\kappa_m \phi_m \sin c\kappa_m \epsilon \right]_0^\epsilon - c^2 \kappa_m^2 \int_0^\epsilon \phi_m \cos c\kappa_m \epsilon d\epsilon. \quad (70)$$

Now in (70) the terms at the limits 0 and ϵ contribute nothing to the emission R_m . The term at the upper limit ϵ can be omitted because at the time $t - \epsilon$ there is no longer any correlation with the first factor on the right-hand side of (69) which refers to the time t . At the lower limit $\epsilon = 0$ we have on the right of (70) only the term $-\frac{d\phi_m}{d\epsilon}$ or $\frac{d\phi_m}{dt}$. This contributes nothing to R_m because the average values of $\phi_m \frac{d\phi_m}{dt}$ and $\frac{d\phi_m}{dt} \frac{d^2 \phi_m}{dt^2}$ are both zero.

Hence

$$R_m = \frac{c^2}{\kappa^2 + \kappa_m^2} \left(\kappa^2 \phi_m - \frac{1}{c^2} \frac{d^2 \phi_m}{dt^2} \right) \int_0^\epsilon \phi_m(t-\epsilon) \cos c\kappa_m \epsilon d\epsilon \quad (71)$$

Reasoning similar to that which gives the reduction from (69) to (70) shows that the average value of R_m at time t is

$$R_m = c^2 \phi_m \int_0^\epsilon \phi_m(t-\epsilon) \cos c\kappa_m \epsilon d\epsilon \quad (72)$$

A result independent of κ . The average total emission is

$$c^2 \iint_{2n} f \phi_m \int_0^\epsilon \phi_m(t-\epsilon) \cos c\kappa_m \epsilon d\epsilon dV_{2n} \quad (73)$$

And the equilibrium of radiation involves that the expression (73) be equal to A_m in (66). Hence

$$\begin{aligned} E_\lambda \iint_{2n} (f, \phi_\lambda) \int_0^\epsilon \phi_\lambda(t-\epsilon) \sin \left(\frac{2\pi c}{\lambda} \epsilon \right) d\epsilon dV_{2n} \\ = - \frac{16\pi^2 c}{\lambda^5} \iint_{2n} f \phi_\lambda \int_0^\epsilon \phi_\lambda(t-\epsilon) \cos \frac{2\pi c}{\lambda} \epsilon d\epsilon dV_{2n}. \quad (74) \end{aligned}$$

Writing as before ϕ_λ for ϕ_m and λ for $2\pi\kappa_m^{-1}$. If it is assumed that the distribution function f depends merely upon the energy H , then

$$\begin{aligned} (f, \phi_\lambda) &= \frac{df}{dH} \sum_{r=1}^{r=n} \left(\frac{d\phi_\lambda}{dp_r} \frac{dH}{dq_r} - \frac{d\phi_\lambda}{dq_r} \frac{dH}{dp_r} \right) \\ &= - \frac{df}{dH} \sum_{r=1}^{r=n} \left(\frac{d\phi_\lambda}{dp_r} \frac{dp_r}{dt} + \frac{d\phi_\lambda}{dq_r} \frac{dq_r}{dt} \right) \\ &= - \frac{df}{dH} \frac{d\phi_\lambda}{dt}. \end{aligned}$$

And on integration by parts since the average value of

$$\frac{d\phi_\lambda}{dt} \int_0^\epsilon \phi_\lambda(t-\epsilon) \sin \left(\frac{2\pi c}{\lambda} \epsilon \right) d\epsilon = - \frac{2\pi c}{\lambda} \phi_\lambda \int_0^\epsilon \phi_\lambda(t-\epsilon) \cos \left(\frac{2\pi c}{\lambda} \epsilon \right) d\epsilon$$

(74) becomes

$$\begin{aligned} E_\lambda \iint_{2n} - \frac{df}{dH} \phi_\lambda \int_0^\epsilon \phi_\lambda(t-\epsilon) \cos \left(\frac{2\pi c}{\lambda} \epsilon \right) d\epsilon dV_{2n} \\ = \frac{8\pi}{\lambda^4} \iint_{2n} f \phi_\lambda \int_0^\epsilon \phi_\lambda(t-\epsilon) \cos \left(\frac{2\pi c}{\lambda} \epsilon \right) d\epsilon, \quad (75) \end{aligned}$$

or if f varies as $e^{-\frac{H}{R\theta}}$,

$$E_{\lambda} = 8\pi R\theta\lambda^{-4} \quad . \quad . \quad . \quad . \quad . \quad (76)$$

§8. ABSORPTION AND REFRACTION OF A SIMPLE HARMONIC WAVE-TRAIN.

The method of normal functions so far used gives no information as to the behaviour of a simple harmonic wave-train advancing into the medium. The defect must be supplied before any theory of the distribution of energy can be brought to the test of experiment. I shall show how the refractive index, absorption, and rotation of the plane of polarization can be expressed in terms of functions involving f the distribution-function.

The equation for F_1 is as before

$$\left(\nabla^2 - \frac{1}{c^2} \frac{d^2}{dt^2}\right) F_1 = \frac{1}{c^2} \frac{d^2}{dt^2} F_0 - \kappa^2 F_0, \quad . \quad . \quad . \quad (28)$$

where
$$(\nabla^2 - \kappa^2) F_0 + 4\pi \frac{\rho \mathbf{u}}{c} = \nabla \left(\frac{1}{c} \frac{d\phi_0}{dt} \right) \quad . \quad (24)$$

$$\text{Div. } F_1 = 0. \quad . \quad . \quad . \quad . \quad (18)$$

Suppose a simple harmonic wave-train moves along the axis of z so that F_1 is a function of z and t only. Then (18) shows that the component of F_1 normal to the wave-front is zero,

$$F_1 \equiv (F_1, G_1, 0) e^{ipt - inz - kz} \quad . \quad . \quad . \quad . \quad (77)$$

This value must finally be supplemented by a conjugate imaginary.

(28) and (24) give

$$\begin{aligned} \left(\frac{d^2}{dz^2} - \kappa^2\right) \left(\frac{d^2}{dz^2} - \frac{1}{c^2} \frac{d^2}{dt^2}\right) F_1 &= \left(\kappa^2 - \frac{1}{c^2} \frac{d^2}{dt^2}\right) \frac{4\pi\rho\mathbf{u}}{c}, \\ &- \left(\kappa^2 - \frac{1}{c^2} \frac{d^2}{dt^2}\right) \nabla \frac{1}{c} \frac{d\phi_0}{dt} \quad . \quad . \quad (78) \end{aligned}$$

The term in $\nabla \left(\frac{1}{c} \frac{d\phi_0}{dt} \right)$ depends merely on the atomic structure of the medium. For a plane wave propagated regularly its average value over the wave-front vanishes. Neglecting scattering, therefore, we may replace (78) by

$$\left(\frac{d^2}{dz^2} - \kappa^2\right) \left(\frac{d^2}{dz^2} - \frac{1}{c^2} \frac{d^2}{dt^2}\right) F_1 = \left(\kappa^2 - \frac{1}{c^2} \frac{d^2}{dt^2}\right) \frac{4\pi\rho\mathbf{u}}{c}, \quad . \quad (79)$$

κ^{-1} is the molecular radius. For waves of ordinary light the terms containing κ^2 are very great compared with the others. (79) becomes

$$\left(\frac{d^2}{dz^2} - \frac{1}{c^2} \frac{d^2}{dt^2}\right) F_1 + 4\pi \frac{\rho u}{c} = 0. \quad . \quad . \quad . \quad (80)$$

Or substituting (77) and multiplying by $e^{-ipt+inz}$

$$\left(\frac{p^2}{c^2} + k^2 - n^2 + 2ink\right) F_1 e^{-kz} + 4\pi \frac{\rho u}{c} e^{-ipt+inz} = 0 \quad . \quad (81)$$

$$\left(\frac{p^2}{c^2} + k^2 - n^2 + 2ink\right) G_1 e^{-kz} + 4\pi \frac{\rho v}{c} e^{-ipt+inz} = 0 \quad . \quad (82)$$

Now integrate each of these equations over any finite area of the wave-front and from $z=z_1$ to $z=z_2$. Then (81) becomes

$$\left(\frac{p^2}{c^2} + k^2 - n^2 + 2ink\right) F_1 \int_{z_1}^{z_2} e^{-kz} dv + 4\pi \int_{z_1}^{z_2} \frac{\rho u}{c} e^{i(nz-pt)} dv = 0 \quad . \quad . \quad . \quad (83)$$

and a similar result from (82). It is not the whole irregular motion of the material system with which we are concerned but only that part of it which is caused by the passage of the wave-train. Thus (83) may be rewritten

$$\left(\frac{p^2}{c^2} + k^2 - n^2 + 2ink\right) F_1 \int_{z_1}^{z_2} e^{-kz} dv + 4\pi \delta \int_{z_1}^{z_2} \frac{\rho u}{c} e^{i(nz-pt)} dv = 0 \quad . \quad . \quad . \quad (84)$$

As in our previous notation δ denotes the deviation due to the force F_1 . In order to calculate the last term in (84) we may therefore put in (59)

$$\psi = \int \frac{\rho u}{c} e^{i(nz-pt)} dv, \quad . \quad . \quad . \quad . \quad (85)$$

and

$$\Phi = \int \left(F_1 \frac{\rho u}{c} + G_1 \frac{\rho v}{c} \right) e^{i(pt-nz)-kz} dv. \quad . \quad . \quad (86)$$

Now it is evident that the average value contributed to the last term in (84) by a group of molecules in the volume element dV will be proportional to dV provided that instead of an infinitesimal element of volume we take one large enough to contain a very large number of atoms. Also owing to the presence of the factor e^{-kz} in Φ this amount will decrease with e^{-kz} where z is the distance of

the element from the origin. This assumes that e^{-kz} is sensibly constant throughout dV .

Instead of (85) and (86) consider the functions

$$\psi_1 = \int_3 \frac{\rho u}{c} e^{i(nz-pt)} dv \quad . \quad . \quad . \quad . \quad (87)$$

$$\psi_2 = \int_3 \frac{\rho v}{c} e^{i(nz-pt)} dv \quad . \quad . \quad . \quad . \quad (88)$$

And

$$\Phi = F_1 \psi_{-1} + G_1 \psi_{-2} ;$$

where the integration in (87) and (88) is supposed to be over unit volume of the medium and ψ_{-1} , ψ_{-2} are the conjugates of ψ_1 and ψ_2 . Then (84) becomes

$$\left(\frac{p^2}{c^2} + k^2 - n^2 + 2ikn \right) F_1 \int_{z_1}^{z_2} e^{-kz} dV + 4\pi \delta \psi_1 \int_{z_1}^{z_2} e^{-kz} dV = 0,$$

or
$$\frac{p^2}{c^2} F_1 + (k + in)^2 F_1 + 4\pi \delta \psi_1 = 0 \quad . \quad . \quad . \quad (89)$$

and

$$\frac{p^2}{c^2} G_1 + (k + in)^2 G_1 + 4\pi \delta \psi_2 = 0. \quad . \quad . \quad . \quad (90)$$

And by (59)

$$4\pi \delta \psi_1 = F_1 \Phi_{11} + G_1 \Phi_{12}, \quad 4\pi \delta \psi_2 = F_1 \Phi_{21} + G_1 \Phi_{22},$$

$$\Phi_{11} = -4\pi \iint_{2n} f \sum_{r=1}^{r=n} \frac{d\psi_1}{dp_r} \frac{d}{du_r} \psi_{-1} dV_{2n} - 4\pi \iint_{2n} (f, \psi_1) \int_0^\epsilon \psi_{-1} dt dV_{2n} \quad . \quad . \quad . \quad (91)$$

$$\Phi_{12} = -4\pi \iint_{2n} f \sum_{r=1}^{r=n} \frac{d\psi_1}{dp_r} \frac{d\psi_{-2}}{du} dV_{2n} - 4\pi \iint_{2n} (f, \psi_1) \int_0^\epsilon \psi_{-2} dt dV_{2n} \quad . \quad . \quad . \quad (92)$$

With similar definitions of Φ_{21} and Φ_{22} (89) and (90) reduce to

$$\frac{p^2}{c^2} F_1 + (k + in)^2 F_1 + \Phi_{11} F_1 + \Phi_{12} G_1 = 0 \quad . \quad . \quad (93)$$

$$\frac{p^2}{c^2} G_1 + (k + in)^2 G_1 + \Phi_{21} F_1 + \Phi_{22} G_1 = 0 \quad . \quad . \quad (94)$$

I reserve the further consideration of these results. Where there is no rotation of the plane of polarization

$$\Phi_{12} = \Phi_{21} = 0.$$

Where the medium is isotropic the defining equations (87), (88), (93) and (94) show that $\Phi_{11} = \Phi_{22}$.

§9. RADIATION AND MECHANICS.

It seems to be almost certain that dynamics leads to a distribution of energy in which $\bar{\epsilon}$ varies as $e^{-H/R\theta}$ and there is equipartition of energy. It is perfectly certain that in nature the consequence is avoided. There are three courses, and three only, open to those who would resolve this antinomy:—

(1) They may deny, and this is the most obvious course, that the reasoning of the kinetic theory is sound.

(2) They may assert that the actual distribution of energy is not a temperature distribution. (See Jeans' 'Theory of Gases').

(3) They may resign their belief in dynamics. Those who have gone beyond M. Planck and founded an atomic theory of energy have made even this sacrifice.

The difficulties of kinetic theory lie in the use it is compelled to make of the rules of probability. And this is of its essence. Where the senses present to us a body whose properties have been through a longer or shorter time unchanged, the kinetic hypothesis sees myriads of atoms or molecules in rapid and always varying motion. The observed absence of change is nothing but a gross or average effect due to the enormous number of the changing parts. It is only by counting chances and reckoning averages that the irreversible movement of heat is reconciled with reversible laws of motion. Those who of our three alternatives choose the first will certainly suggest that the paradoxes in which the theory is landed are due to the use it makes of the science of probabilities, and not to any inadequacy in the science of mechanics to explain the facts of heat and radiation.

A material system which is so enclosed that it cannot lose heat by radiation or conduction will in the end come to a state in which the temperature is steady and the same at every point. That is the great fact to be explained by mere dynamics. No matter what the initial conditions, it is to be shown that the laws of motion are always adequate to produce the observed result. These laws are expressed most generally by Hamilton's equations of motion deduced from the principle of least action. Starting from any initial values of the coordinates, the q 's and p 's, we are compelled to assert that on the average the system will have the properties, whatever they may be, of a body in temperature equilibrium. As in (2) write

$$dV_{2n} = dq_1, dq_2 \dots dq_n, dp_1, dp_2 \dots dp_n.$$

It is well known that dV_{2n} is a differential invariant.

At any time we start a number of systems proportional to dV_{2n} and having their coordinates in the $2n$ 'ple element dV_{2n} . This distribution is invariant and in each system the state of temperature equilibrium is reached. I have shown (Phil. Mag., Jan. 1911, p. 18) that we need only assume that a finite value of H involves finite momenta. Then by averaging over all these systems having the same total energy H , it can be shown that any degree of freedom has the same kinetic energy as any other. This does not indeed prove that in any one body at a constant temperature there is equipartition of the kinetic energy. For conceivably the same total energy H may be distributed in different ways between kinetic and potential and result in different temperatures. But it is a result impossible to reconcile with the fact expressed in such a formula for the complete radiation as M. Planck's. For there it appears that the smaller wave-length has the lesser energy at all temperatures whatever. No process of averaging over bodies in temperature equilibrium can assign the same energy to the two wave-lengths.

The only escape from this reasoning is to suppose that there are certain values of the coordinates which cannot occur in nature. But the principle on which these are excluded must be dynamical. For example, a vortex theory of matter would allow only such distributions as have throughout the same circulation in corresponding circuits. Unless some such ground for ruling out particular initial conditions can be given, dynamics is confessed to be unequal to the task of bringing about temperature equilibrium. But so far as I am able to see, constant circulation involves merely a reduction in the number of the degrees of freedom. Thus in the case of a mass of liquid moving irrotationally it makes the motion of any point in the interior determinate when the motion of the surface is given. The degrees of freedom of a gravitating spherical volume of water for example, become an enumerable infinity of normal vibrations for small disturbances from the spherical shape.

Where an atomic theory of matter is retained, it seems impossible to see how any configuration can be excluded, and here dynamics leads to the paradoxes of equipartition. Where matter is continuous it may be pleaded that the contradiction is not certain. But to say that the distribution of energy depends upon the dynamics of a continuous fluid and that no light is thrown upon it by anything that happens in a system having only a finite number of degrees

of freedom, is to make the problem practically insoluble. The first alternative is no longer open. The reasoning of the kinetic theory is soundly based on the laws of dynamics, and the postulate of an essentially positive energy.

Of those who have chosen the second of our three alternatives and deny the reality of temperature equilibrium, it is scarcely unjust to say that they prefer the dynamical theory to the physical facts it has failed to explain. I do not understand their theory. Wherever there is less energy than Rayleigh's formula would require they suspect that it escapes all enclosures designed to trap it and never appears in what is falsely supposed to be the complete black body radiation. Then, of course, the Fourth Power law and Wien's law deduced by thermo-dynamics have no rational basis, the success of the reasoning by which they were reached is a mere accident. For complete radiation as ordinarily understood is not radiation in temperature equilibrium at all. This is bad enough in theory, but further it is contrary to fact to say that the defect of radiation for ordinary light-waves is due to the transparency of the enclosure to them. It is due to the enormously greater absorbing power of the body which emits these waves than we should expect were the ratio of absorption to emission given by Rayleigh's formula. (See *Phil. Mag.* xxii. pp. 71, 72, 1911). The light-waves are absorbed and the energy reappears at once as heat, the complete radiation is what it is always assumed to be—the result of a balanced radiation and absorption. If we postulate some process by which the absorption is effected which is not equally involved in the radiation then we are resigning dynamics. I have shown in this paper and in my last that the pressure of radiation for example will produce no deviation from the formula (76).

There remains, it appears to me, nothing but to embrace the last alternative and resign our belief in the universal validity of dynamics. Jeans (*Phil. Mag.* xx. p. 943, 1910) has indeed argued that any system of laws of motion involves the doctrine of equipartition. I offer the following equations of motion as a test of his conclusion.

Let $q_1 \dots q_2 \dots q_n$ be the coordinates of position of a dynamical system and $p_1 \dots p_2 \dots p_n$ be the momenta. The equations which replace Hamilton's are to be

$$\phi_r \frac{dq_r}{dt} = \frac{dH}{dp_r}, \quad \phi_r \frac{dp_r}{dt} = -\frac{dH}{dq_r} \quad (r=1, 2 \dots n) \quad . \quad (95)$$

H may be any function not containing the time explicitly ;

in particular we may if we please take

$$H = \sum_{r=1}^{r=n} \frac{1}{2} p_r^2 + V,$$

where V involves the q 's only.

$$\frac{\partial H}{\partial t} = \sum_{r=1}^{r=n} \frac{dH}{dp_r} \frac{dp_r}{dt} + \frac{dH}{dq_r} \frac{dq_r}{dt} = 0.$$

So that H is a constant. Let

$$\phi_r = f_{(r1)}, f_{(r2)} \dots f_{(rs)} \dots f_{(rn)} (s=1, 2 \dots n), \quad (96)$$

where $f_{(rs)} = f_{(sr)}, \dots \dots \dots (97)$

and $f_{(rs)}$ is a function of p_r, q_r , and p_s, q_s only.

The distribution of systems in which the number in the $2n$ 'ple volume element dV_{2n} is ρdV_{2n} will be invariant of

$$\frac{d}{dt} (\rho dV_{2n}) = 0,$$

which gives the ordinary equation of continuity

$$\sum_{r=1}^{r=n} \left\{ \frac{d}{dq_r} \left(\rho \frac{dq_r}{dt} \right) + \frac{d}{dp_r} \left(\rho \frac{dp_r}{dt} \right) \right\} = 0, \quad (98)$$

or

$$\sum_{r=1}^{r=n} \left\{ \frac{d}{dq_r} \left(\frac{\rho}{\phi_r} \right) \frac{dH}{dp_r} - \frac{d}{dp_r} \left(\frac{\rho}{\phi_r} \right) \frac{dH}{dq_r} \right\} = 0. \quad (99)$$

This equation can be satisfied by taking

$$\rho = \prod_{r=1}^{r=n} \prod_{s=1}^{s=n} f_{rs}$$

so that ρ is the product of the distinct functions $f_{(r,s)}$ each taken once. With this value of ρ it follows from (96) and

(97) that $\frac{\rho}{\phi_r}$ does not involve p_r or q_r and each term in (98) vanishes identically.

The equipartition of the kinetic energy would require

$$\iint_{2n} p_r \frac{dH}{dp_r} \rho dV_{2n} = \iint_{2n} p_s \frac{dH}{dp_s} \rho dV_{2n}.$$

And this need not be so.

By taking only two coordinates p_1 and p_2 , writing

$$H = \frac{1}{2} (p_1^2 + p_2^2) \\ f_{11} = e^{+\alpha p_1^2}, \quad f_{12} = 1, \quad f_{22} = e^{+\beta p_2^2},$$

it may easily be proved that the ratio in which the energy

H is divided between the two degrees of freedom depends on the amount of energy to be divided, that is upon the temperature.

March 14, 1911.

Note added January, 1912.

It is of course true that the equations (95) can now be reduced to Hamilton's by putting

$$p_1' = \int e^{ap_1^2} dp_1, \quad p_2' = \int e^{bp_2^2} dp_2.$$

The theorem of equipartition of kinetic energy gives equal average values to $p_1' \frac{dH}{dp_1'}$ and $p_2' \frac{dH}{dp_2'}$. (See *Phil. Mag.* Jan. 1911, p. 48). Here, however, H is no longer a quadratic function of the new momenta and the kinetic energy defined as the sum

$$\frac{1}{2} p_1' \frac{dH}{dp_1'} + \frac{1}{2} p_2' \frac{dH}{dp_2'}$$

is not a part of the true energy H .

Nor does the classical theory of the æther require equipartition of the radiant energy in the way Rayleigh's formula would indicate. That consequence follows only if æther and matter together form a dynamical system whose laws of motion are deduced from a single formula for the action. Now very much less than this will serve as a mechanical foundation for thermodynamics as Einstein (*Annalen der Physik*, 1903, xi. pp. 170-187) had already shown. In fact let it be granted that there are:—

(1) Continuous laws of motion by which the state of the system at any instant can be deduced from its state at any other.

(2) A unique energy integral of the form

$$H = \text{constant},$$

H being independent of the time.

(3) A function ρ defined by the configuration at time t such that

$$\frac{d}{dt}(\rho dV_{2n}) = 0.$$

It can easily be proved that if there is only one energy H the most general solution ρ_1 for ρ is

$$\rho_1 = F(H)\rho;$$

where ρ is any solution whatever. Let it be granted that

the statistical method applies to æther with its infinity of degrees of freedom. As in this paper the æthereal energy falls into the normal vibrations determined by the volume enclosed. Where there is no matter,

$$\rho = \prod_{m=1}^{m=\infty} f(H_1)f(H_2) \dots f(H_m) \dots \quad (100)$$

Here H_m is the energy of the m th æthereal degrees of freedom p_m, q_m , where

$$\frac{dp_m}{dt} = -\kappa_m^2 q_m, \quad \frac{1}{c^2} \frac{dq_m}{dt} = p_m, \quad H_m = \frac{c^2}{2} p_m^2 + \frac{1}{2} \kappa_m^2 q_m^2.$$

Where there is no matter present $H_1, H_2 \dots H_m$, &c. are all constant, for the normal vibrations do not interact, and there is nothing to determine $f(H_m)$. That function does not, however, necessarily reduce to a constant unless all the laws of motion are deduced from a single action formula. As in this paper we may suppose a very large volume of "æther" containing matter only for the purpose of bringing about a temperature distribution. (100) now no longer gives the complete expression for the function ρ . But now suppose the material system defined by $2n$ coordinates

$$\rho = F_{(M)} \times \Phi_{(M, A)} \times \prod_{m=1}^{m=\infty} f(H_m).$$

And for the purely material interactions

$$\frac{d}{dt} (F_M dv_{2n}) = 0.$$

Here F_M is a function containing only the material co-ordinates. $\Phi_{(M, A)}$ contains both material and æthereal degrees of freedom, and since these interact only slightly when the volume of æther is made very large, we may make $\Phi_{(M, A)}$ tend towards unity by sufficient increase of that volume. If the ordinary statistical argument be now applied, it can be shown (see Jeans' 'Dynamical Theory of Gases') that the infinitely probable distribution of energy is one in which

$$\rho_1 = \prod_{m=1}^{m=\infty} e^{-hH_m} f(H_m),$$

and the average value of H_m say $\overline{H_m}$ is given by

$$\overline{H_m} = -\frac{d}{dh} \left\{ \text{Log} \int_0^\infty e^{-hH_m} f(H_m) dH_m \right\}. \quad (101)$$

All observations of complete radiation show that H_m falls off when h is large, that is when the temperature is small, in some such ratio as e^{-a_h} where a is inversely as the wavelength. Hence

$$\int_h^\infty \overline{H}_m dh$$

is finite and by integration of (101) it follows that $\psi(h)$ bears a finite ratio to $\psi(\infty)$ where

$$\psi(h) = \int_0^\infty e^{-hH_m} f(H_m) dH_m.$$

This, it can easily be seen, is impossible if $f(H_m)$ is not somewhere infinite. Planck has in fact, while retaining the formula (101), supposed that $f(H_m)$ is zero except at a set of points distributed at equal intervals where it becomes infinite.

CONCLUSION.

It now appears that with no continuous laws of motion is it possible to account for the actual distribution of energy. The proof, however, involves the assumption that the statistical method applies to the æther with its infinity of degrees of freedom. Since this paper was completed I have succeeded in extending the direct calculation of emission and absorption to matter obeying any continuous laws of motion whatever. That I reserve for another paper; in this the direct method has shown that for any material system equipartition follows if the principle of least action is assumed.

January 29, 1912.

XLVIII. *The Photoelectric Properties of Thin Metal Films.*

By J. ROBINSON, M.Sc., Ph.D., Demonstrator in Physics at the University of Sheffield *.

THE photoelectric effect of thin metal films on quartz has been investigated by Kleeman † and by Stuhlmann ‡, both of whom found a difference in the effects produced by incident and emergent lights. For thin films the emergent light produces a larger ionization current than incident light. Stuhlmann showed further that the reverse is the case for thick films. Both investigators worked with films in air at atmospheric pressure. Kleeman also made a measurement at a low pressure.

* Communicated by the Author.

† Kleeman, Proc. Roy. Soc. lxxxiv. 1910, p. 93.

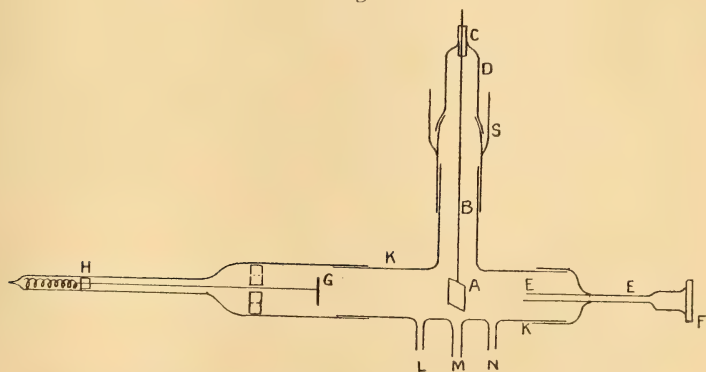
‡ O. Stuhlmann, Phil. Mag. xx. 1910, p. 331.

It has been found that the photoelectric properties of metal films vary much under different circumstances, and depend especially on whether they have been in the atmosphere or not. Consequently, in the experiments described in the following pages, care was taken that the films were deposited at a low pressure in the tube in which measurements were to be made, and immediately after depositing, as high a vacuum as possible was obtained, and maintained during the course of some of the experiments. Measurements were made of the photoelectric velocities and currents for incident and emergent light.

Description of the Apparatus.

The quartz plate A ($1\frac{1}{2}$ mm. thick) was attached to a thick brass rod B, which was fixed by sealing-wax through

Fig. 1.



an amber plug C, which in its turn was fixed into one part D of a ground joint S. By means of this ground joint the quartz plate A could be made to take up any angle with regard to the direction of the light through the tube EE. This tube was narrow so as to admit only a thin beam of light. The quartz plate F closed the tube E. G was a platinum electrode attached rigidly to a rod, at the other end of which was an iron ring H. By applying an electro-magnet from outside to this iron ring, the system HG could be moved along the tube KK. Before the quartz plate A and the platinum electrode G were inserted, the walls of the tube KK were coated thickly with platinum by stretching a platinum wire through the tube, and passing a current between it as cathode, and a wire in one of the side tubes

LMN at a low pressure. A wire passing through the tube L was made to touch the walls so that the potential of the latter could be controlled. The tube M was used for connecting to the mercury-pump, and through N a wire protruded a short distance into the tube K. This wire was used as anode when the current was passed from the platinum electrode G as cathode to deposit a film on the quartz plate A.

Before this was done, G was kept as far as possible away from A, and the current passed for a long time to drive out some of the occluded gas. Then G was moved up to about 1 cm. from A and the film deposited.

The rod B was connected in the ordinary way to one pair of quadrants of a Dolezalek electrometer. In making measurements of the velocities of the electrons, all stray wires, L, M, and the platinum electrode G were earthed, so that the thin film was in an earth-connected cylinder. The maximum potential taken up by the film under the action of ultra-violet light was measured, when it was turned to face the light (incident), and when it was turned away from the light (emergent). The velocity v of an electron is connected with this maximum potential V by the formula $\frac{1}{2}mv^2 = eV$.

Scales were pasted around the two portions of the ground joint so as to show exactly what position the quartz plate occupied. A quartz mercury lamp was used as source of light.

The measurements of the photoelectric current were made by shunting the pairs of quadrants of the electrometer by a high resistance. This resistance was made by depositing platinum on glass. It was found that if the vessel in which this was done was pumped out as far as possible and sealed off, a very constant high resistance was obtained, which is very suitable for the present purpose. The currents were measured for different fields between the film and the walls of the vessel, which fields were obtained by charging the walls to different potentials.

The relative thicknesses of the films are given in terms of the lengths of time taken to deposit them.

The last column gives the ratio of the emergent velocity to the incident velocity. It will be noticed that for the films 40 minutes and 50 minutes, different values are given for the actual velocities. These different values for the same film were obtained under different conditions. The measurements were always made at the highest vacuum it was possible to obtain, but on a few occasions it was necessary to let air into the tube. On pumping out again, it was

TABLE I.

Measurement of the velocities of the electrons produced by incident and emergent lights.

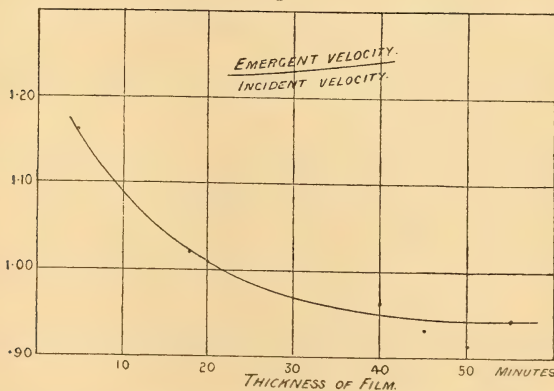
Relative thickness of film.	Emergent Light.		Incident Light.		$\frac{C}{D}$.
	Maximum Potential attained by film. A.	Corresponding velocity, $\times 10^7 \frac{\text{cm.}}{\text{sec.}}$ C.	Maximum Potential attained by film. B.	Corresponding velocity $\times 10^7 \frac{\text{cm.}}{\text{sec.}}$ D.	
5 minutes...	0.86 volt	2.76	0.64 volt	2.37	1.16
8 " ...	0.80	2.66	0.65	2.40	1.11
18 " ...	0.84	2.73	0.80	2.66	1.02
40 " ...	1.56	3.71	1.57	3.73	0.99
	1.20	3.26	1.36	3.47	0.94
	1.75	3.94	1.95	4.15	0.95
	1.63	3.86	1.85	4.05	0.95
45 " ...	1.99	4.20	2.32	4.53	0.93
50 " ...	2.19	4.40	2.77	4.95	0.89
	1.33	3.43	1.62	3.77	0.91
55 " ...	1.53	3.68	1.75	3.94	0.93
	1.91	4.11	2.16	4.37	0.94

Mean
= 0.96

Mean
= 0.91

Fig. 2 shows graphically the relation between $\frac{C}{D}$ and the thickness of the film.

Fig. 2.



found that the actual velocities had diminished both for incident and emergent light. On standing in a vacuum for some time the velocities increased again, but not to exactly the same values as before letting in air. It will be noticed that the ratio of the emergent to incident velocities has not varied much, although the actual velocities varied.

This seems to show that occluded gas in the film influences the actual magnitudes of the velocities, though not the ratio for the incident to emergent effects. The values given for the velocities represent steady values which are only obtained some time after the film was deposited. Immediately after a film has been deposited the velocities vary considerably, but more for incident than for emergent light. A constant ratio was only obtained some time after depositing. Frequent attempts were made to find whether it was possible to eliminate these initial variations by passing the current for a long time before depositing the film, so as to get rid of occluded gas from the platinum electrode, but so far it has not been found possible to do this.

Fig. 3.—Film of 5 minutes.

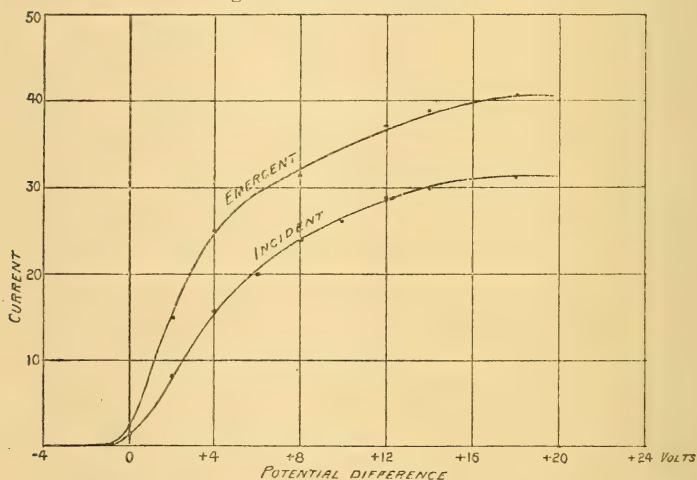
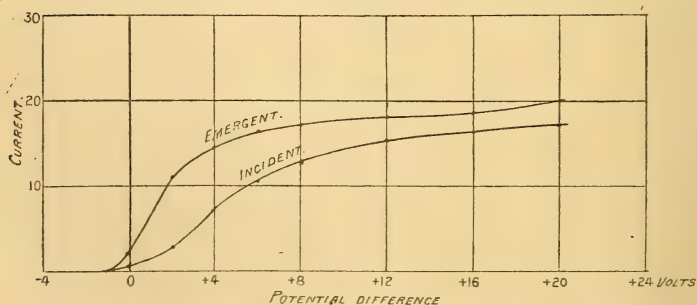


Fig. 4.—Film of 8 minutes.



The results of Table II. are shown graphically in figs. 3-6. It is seen that in every case the photoelectric current

TABLE II.
Photoelectric Currents produced by Incident and Emergent Lights.

Potential of walls.	Film of 5 minutes.		Film of 8 minutes.		Film of 18 minutes.		Film of 55 minutes.	
	Emergent effect.	Incident effect.	Emergent.	Incident.	Emergent.	Incident.	Emergent.	Incident.
- 8 volts. ...			0	0	0	0	- 0.2	- 0.2
- 6	0	0		0			0	0
- 2	2	1	2	0.5	2.5	1	7	9.5
+ 2	15	8	11	2.5	19	5	15	22
+ 4	25	16	14.5	7.5	21.5	14	16	33
+ 6	29.5	20	16.5	10.5	23	18.7	15	39.5
+ 8	31.5	24	17	12.5	24.2	21.5	17	46.5
+ 10	34.5	26		15.5				51.5
12	37	29	18		25.5	23	15	55.8
14	39	30					18	57
16			18.5	16.5	26.2	24.2		57.8
18	40.5	31						59
20			20		28.8	25.7	18.5	59
24				17	30	27.8		

The unit of current varies from film to film.

approaches a maximum value as the potential difference between the film and the walls of the vessel increases, so as to drive electrons away from the film. Also in all but one case it is noticed that there is no inverse photoelectric effect,

Fig. 5.—Film of 18 minutes.

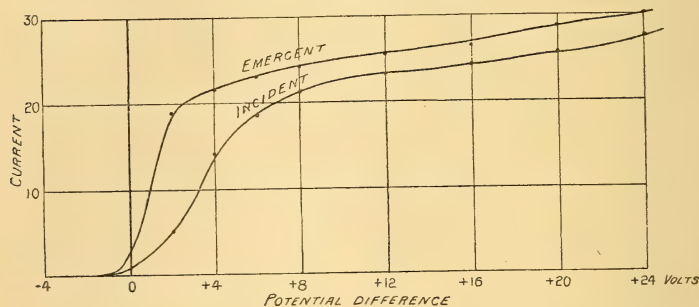
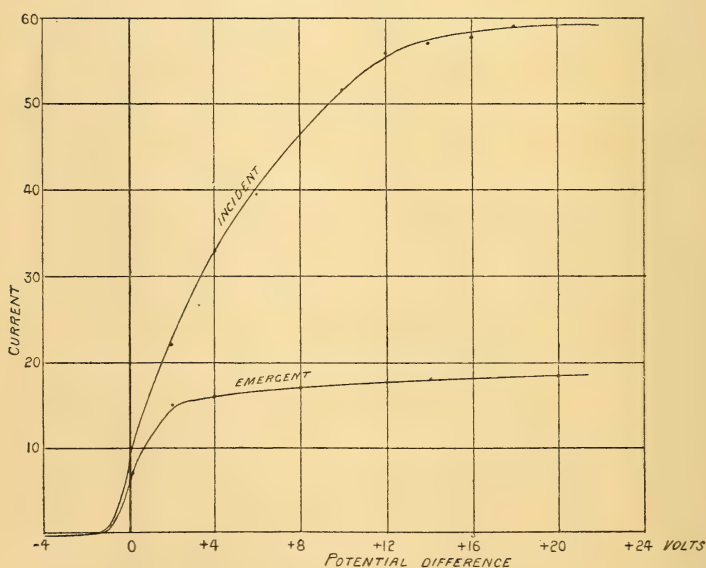


Fig. 6.—Film of 55 minutes.



which shows that the influence of reflected light can be neglected. Here, again, as in the case of the velocities, an influence of the thickness of the film is noticeable. For thin films the maximum photoelectric current is larger for emergent than for incident light, and for thick films the reverse is

the case. In the following table the ratio of the maximum currents is shown in relation to the thickness of the film.

TABLE III.

Relative thickness of film.	Maximum current.		$\frac{A}{B}$.
	Emergent. A.	Incident. B.	
5 minutes	40	31	1.29
8 „	18	16	1.12
18 „	30	27	1.11
55 „	18	59	0.31

Discussion of Results.

Velocities.—Fig. 2 shows that for thin films the velocities of the electrons for emergent light are greater than those for incident light, and that for thick films the reverse is the case. The velocities measured were the maximum velocities in each case, which, according to Ladenburg *, refer to the shortest wave-lengths of light used. Thus one particular wave-length of light produces quicker electrons for emergent than for incident light, when thin films are used, and *vice versa* for thick films.

It was thought that possibly the results for thick films might be due to some selective absorption of light by them. Thus if the shortest wave-lengths are absorbed completely before the light has penetrated far into the film, then the velocities of the emergent electrons will be smaller than those of the incident. It was not found possible to substantiate this possibility by taking photographs of the spectrum of the lamp used. A Hilger quartz spectroscope was used and photographs taken :—

- 1st. With nothing between the lamp and the spectroscope.
- 2nd. With a film of 18 minutes deposit before the slit.
- 3rd. „ „ 55 „ „

In each case a number of exposures of different lengths of time were made, and although a general absorption of light by the films was observed, yet it was not possible to detect any selective absorption. The shortest wave-lengths

* *Phys. Zeit.* 1907, p. 590.

could be photographed through the thickest film used. The wave-length of this line was 2302. The spectrum was a line spectrum.

Currents.—The results obtained from the measurements of currents are :—

1. That for thin films the maximum emergent current is larger than the maximum incident current, and *vice versa* for thick films.

2. For emergent light, the current rises rapidly with potential difference at first, and approaches its maximum value for a small value of this potential. The turning-point of the curves between the rapid increase and the slow increase to the maximum value, is at about 2 volts for the 18-minute and the 55-minute films, and at about 4 volts for the 8-minute film. For incident light, the rise of the current with the potential difference is not so great at first as for emergent light, and the turning-points to the saturation-values are at much higher potentials, of the order 8-12 volts.

These results show that light assists electrons to leave a metal more in the direction of the light than in the opposite direction for thin films, but when the films are thick the reverse is the case.

Without attempting to explain the whole phenomena, attention might be called to the difference in the form of the curves for incident and emergent currents (figs. 3-6). This difference cannot, I think, be explained by a dissymmetry in the tube.

An explanation of the form of the curve for thick metals was put forward by Ladenburg and Markau *. They supposed that the same number of electrons leave an electrode no matter what the potential difference between it and the receiving electrode is. The fact that a certain potential difference is necessary in order to obtain the maximum current, they explain as being due to electrons being reflected from the receiving electrode and getting back to the emitting electrode when the potential difference is small. If this is the case, then the form of the curve ought to be the same for incident and emergent light. Again, in the present experiments the receiving electrode is the walls of the vessel, and so is perpendicular to the emitting electrode, so that any reflected electrons ought to go to other parts of the walls and not get back to the film.

The original explanation of the form of the curve given by Lenard †, that a certain potential difference is necessary

* *Verh. d. deutsch. Phys. Ges.* 1908, n. 14, p. 562.

† *Ann. der Phys.* viii. 1902, p. 149.

to drive the electrons away from the surface, is more in harmony with the present experiments. According to this view a larger potential difference is necessary to drive electrons away from a film for incident light than for emergent light, thus showing that the direction of the light has something to do with the emission of electrons.

Approximate values of the actual thicknesses of the films used can be calculated in the following way :—

Drude's values * for the absorption coefficient and reflexion coefficient for platinum for sodium light is $45,000 \text{ mm}^{-1}$ and $\cdot 70$ respectively. It is doubtful whether the same values hold for thin films, but an approximation can be made to the true state of affairs by assuming these values for the whole spectrum and for thin films. The thickest film used (55 minutes) let through about 20 per cent. of the light which fell on it. This was measured photometrically and also estimated from the spectra. 30 per cent. of the light falling on the film enters it, and thus 10 per cent. is absorbed. This means that a film of 55 minutes deposit absorbs $\frac{1}{3}$ of the light which enters it. The intensity of light falls off according to an exponential law. On plotting the curve $y = e^{-45,000x}$ it is found that an absorption of 33.3 per cent. corresponds to a thickness of 10^{-6} cm .

The thicknesses of the other films can be readily calculated once the thickness of one has been determined.

I have great pleasure in recording my best thanks to Prof. Hicks and Dr. S. R. Milner for the interest they have taken in this work, and for much valuable advice in connexion with it.

University of Sheffield,
Dec. 6, 1911.

XLIX. *The Virial of a Mixture of Ions.* By S. R. MILNER, D.Sc., Lecturer in Physics, The University, Sheffield†.

THE problem considered in this paper is the determination of the average virial of a mixture of $N +$ and $N -$ ions contained in a volume V , on the assumption that every $+$ ion repels every other $+$ ion, and attracts every $-$ ion, with a force q^2/r^2 , where r is the distance between the pair of ions considered, and q the ionic charge. The following statement defines both the average virial and also the strict theoretical method of calculating it :—For a

* Wied. Ann. 1890, Bd. xxxix. p. 481.

† Communicated by the Author.

particular configuration of the ions, take for a pair of ions the product of their mutual force into the distance between them, reckoning it + when the ions are like, and - when they are unlike; sum this quantity for every pair which can be formed out of the $2N$ ions, we get the virial for this configuration. Multiply this sum by the probability of the occurrence of this configuration, and sum up for every possible configuration of the ions in the volume, and we get the average virial. The virial here considered is that due to the electrical forces only: it is reckoned + when repulsive, and it is the same as the potential energy of the ions, if we understand by this the work which the electrical forces are capable of performing as the ions are moved to infinite distances apart.

When the average virial is known, the pressure of a gaseous mixture is easily determined by Clausius' theorem, or in electrolytes the osmotic pressure by thermodynamical reasoning, and the result has important applications to the dissociation theory of electrolytes.

If the ions were uncharged we should be justified in assuming that their distribution in the volume V was a random one, for we have no data for asserting it to be anything else. (By a random distribution it is meant that on taking an instantaneous view of the system any given ion is just as likely to be found in any one place in the volume as in any other.) If the distribution were a random one when the ions are charged, the virial might be either + or - for any particular configuration, but the average over all cases must necessarily be zero; for the ions existing in any two given positions are just as likely to be of like as of unlike sign, and so the term which they contribute to the whole sum is necessarily zero on the average*. The distribution will, however, not be random when the ions are charged; the effect of the inter-ionic forces will be to increase the chance of the occurrence of those configurations which have a negative virial, and to diminish the chance of the occurrence of those configurations which have a positive one. The average virial is consequently negative.

It has been proved by Boltzmann† (*Vorlesungen über Gastheorie*, 1898, Part II. p. 137) that if $P(E)$, $P'(E')$

* This is only strictly true when N is so large that the difference between N and $N-1$ is negligible.

† It should be mentioned that the statement in the text represents a slight extension of Boltzmann's actual theorem. Boltzmann stated the theorem only for a "constellation" or group of molecules in the system, but it seems to me there is no reason why we should not extend the group so as to comprise the whole system, if we so desire

stand for the probabilities of the occurrence of configurations of which the potential energies are E, E' respectively in a system of molecules where intermolecular forces exist, and $\bar{P}, \bar{P}'$ stand for the probabilities of the occurrence of the same configurations in the same system of molecules if there were no intermolecular forces, then

$$\frac{\bar{P}(E)}{\bar{P}'(E')} = \frac{P}{P'} e^{-(E-E')/w}, \quad \dots \quad (1)$$

where w stands for the most probable value of the kinetic energy of a molecule. If R is the gas constant, T the absolute temperature, and ν the number of molecules in a gram molecule, then

$$w = \frac{RT}{\nu} \dots \dots \dots (2)$$

In applying Boltzmann's theorem to our system of ions we assume that if there were no inter-ionic forces the distribution of the ions would be a random one; P and $\bar{P}(E)$ will stand respectively for the probabilities of the occurrence of a given configuration in a random distribution, and in the distribution as modified by the electrical forces. Equation (1)

may be written in the form $\frac{\bar{P}(E)}{P} e^{-E/w} = \text{constant}$ for all configurations $=k$, say, hence

$$P(E) = kP e^{-E/w}, \dots \dots \dots (3)$$

where k is a quantity which is independent of E , and is theoretically determined from the consideration that $\sum P(E)$ for every possible configuration of the system must be equal to unity.

We next proceed to determine P , and we shall calculate it for a configuration which is defined as follows:— A_0 is a given ion in the mixture; the nearest ion to it, A_1 , lies in a given elementary volume dv_1 at a distance r_1 away from A_0 ; the second nearest ion to it, A_2 , lies in a volume dv_2 at a distance r_2 away from A_0 ; ... the m th nearest ion A_m lies in a volume dv_m at a distance r_m away from A_0 .

In a random distribution the chance that any individual ion is not at a given instant included in any volume v imagined in the whole volume is $1 - v/V$. The chance that none of the $2N$ ions are in v is therefore

$$\left(1 - \frac{v}{V}\right)^{2N},$$

or, on expansion,

$$1 - \frac{2N}{V}v + \frac{2N(2N-1)}{2! \cdot V^2}v^2 - \dots \dots$$

Since $2N$ is a very large number this is practically identical with

$$e^{-\frac{2N}{V}v}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

so long as v is not a large fraction of the whole volume.

The chance that there does exist an ion in v is

$$1 - \left(1 - \frac{v}{V}\right)^{2N},$$

which reduces to

$$\frac{2N}{V}v, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

if v is infinitesimally small.

Out of a large number of instantaneous views (or "cases") of the given ion A_0 and its neighbours, the fraction of the cases in which the nearest ion is situated in the volume dv_1 at the distance r_1 away from A_0 is given by the chance that there is no ion in the sphere $\frac{4}{3}\pi r_1^3$ described round A_0 as centre, combined with the chance that there is an ion in the given volume dv_1 . We get for this, from (4) and (5), and neglecting the volume of the ion A_0 in comparison with $\frac{4}{3}\pi r_1^3$,

$$e^{-\frac{2N}{V} \cdot \frac{4}{3}\pi r_1^3} \cdot \frac{2N}{V} dv_1 \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The fraction of *these* cases in which the second nearest ion A_2 is situated in dv_2 at distance r_2 from A_0 , is the chance that there is no ion in the shell $\left(\frac{4}{3}\pi r_2^3 - \frac{4}{3}\pi r_1^3\right)$ between A_1 and A_2 , combined with the chance that there is an ion in dv_2 , that is,

$$e^{-\frac{2N}{V} \left(\frac{4}{3}\pi r_2^3 - \frac{4}{3}\pi r_1^3\right)} \cdot \frac{2N}{V} dv_2 \quad . \quad . \quad . \quad . \quad (7)$$

Similarly for the third, fourth, fifth, nearest ions, A_3, A_4, A_5 , right up to the m th, so long as m is not comparable with $2N$. Multiplying together (6), (7), &c., we get for the probability that the nearest ion to a given ion lies in a given elementary volume dv_1 at r_1 , the 2nd nearest in dv_2 at $r_2, \dots$ the m th nearest in dv_m at r_m ,

$$P = e^{-\frac{2N}{V} \cdot \frac{4}{3}\pi r_m^3} \cdot \frac{2N}{V} dv_1 \cdot \frac{2N}{V} dv_2 \dots \frac{2N}{V} dv_m \quad . \quad (8)$$

So far no account has been taken of the sign of the ions in the configuration, but since any ion, say the p th nearest ion, is just as likely to be + as -, the probability of any one order of succession in the signs of the m nearest ions counting outwards from A_0 is the same as that of any other order, and is $1/2^m$.

In order to allow of the introduction of the sign of the charge into the statement of the configuration, we shall write the charge on A_0 as q_0 , on A_1 as q_1 , &c. q_p can be afterwards put $+q$ or $-q$, according as the p th ion is positive or negative. Also let r_{ip} be the distance between A_i the i th nearest ion, and A_p the p th nearest ion to A_0 .

The potential energy of the assumed configuration is given by the following scheme :—

$$\begin{aligned} E = & q_0 q_1 / r_{10}, \\ & + q_0 q_2 / r_{20} + q_1 q_2 / r_{12}, \\ & + q_0 q_3 / r_{30} + q_1 q_3 / r_{13} + q_2 q_3 / r_{23}, \\ & + \dots\dots\dots, \\ & + q_0 q_p / r_{p0} + q_1 q_p / r_{1p} + \dots\dots\dots q_{p-1} q_p / r_{p-1,p}, \\ & + \dots\dots\dots, \\ & + q_0 q_m / r_{m0} + q_1 q_m / r_{1m} + q_2 q_m / r_{2m} + \dots\dots\dots + q_{m-1} q_m / r_{m-1,m}. \end{aligned}$$

which may be written shortly

$$E = \sum_{p=1}^m \sum_{i=0}^{p-1} \frac{q_i q_p}{r_{ip}} \dots\dots\dots (9)$$

The virial of the central ion A_0 with respect to these m ions is

$$U = q_0 q_1 / r_1 + q_0 q_2 / r_2 + q_0 q_3 / r_3 + \dots\dots\dots + q_0 q_m / r_m \dots,$$

or

$$U = \sum_{v=1}^m \frac{q_0 q_v}{r_v} \dots\dots\dots (10)$$

Introducing the values of P and E from (8) and (9) into (3) we get for the probability of the given configuration when the inter-ionic forces are taken into account, and the signs of the ions are specified

$$P(E) = k_m \cdot e^{-\frac{1}{w} \sum_{p=1}^m \sum_{i=0}^{p-1} \frac{q_i q_p}{r_{ip}}} - \frac{2N}{V} \cdot \frac{4}{3} \pi r_m^3 \cdot \frac{2N}{V} dv_1 \cdot \frac{2N}{V} dv_2 \dots\dots\dots \frac{2N}{V} dv_m, \quad (11)$$

where k_m is written for $k \times \frac{1}{2^m}$.

It will be observed that in equation (11) what is stated is not the probability of a given configuration of the whole of the $2N$ ions, but only that of a certain number m of ions nearest to an arbitrarily chosen one A_0 . The strict theoretical method of solving the problem would be, as has already been mentioned, to calculate $P(E)$ and E for a given configuration of the whole of the $2N$ ions; the average virial $\bar{E}$ would then be obtained by summing up the quantity $E.P(E)$ for every possible configuration of the ions in the volume V . Instead of doing this we shall adopt a simpler process which gives the same thing in the end. We first determine the average virial on the ion A_0 of all the m nearest ions to it, the average being taken over all possible positions and signs of each of these; *i. e.*, we sum up the quantity $U.P(E)$ for all possible configurations of the m ions. If we can obtain the limiting value $\bar{U}$, which this approaches as m becomes infinite, we have the average virial on A_0 of all the remaining ions in the volume. We can then write the total average virial of all the $2N$ ions in the volume in the form $\bar{E} = N\bar{U}$ (the 2 disappears since the virial of each pair of ions is only to be reckoned once).

A certain difficulty with regard to equation (11) may with advantage be discussed here. Boltzmann, in deducing the theorem on which (11) is founded, first proves it for the case of two molecules close together under the condition that the forces exerted between them and the remaining molecules are negligible, and he then points out that the theorem may be extended to any number of molecules close together under the same conditions. Now in the case of ions, where the forces vary comparatively slowly with the distance, the forces between a group of a finite number of nearest ions and the remaining ions in the volume will not be in general negligible. Hence, while the theorem is doubtless valid for the whole of the $2N$ ions taken together, it is open to question whether it is justifiable to apply it in the way in which it has been here done to a group consisting of a finite number of nearest ions only. If it is not, then (11) must be looked on as merely an approximation to the true expression. I think it is probable, indeed, that (11) is only an approximation when m is finite, for the reason that, by the presence in

it of the factor $e^{-\frac{2N}{V} \cdot \frac{4}{3} \pi r_m^3}$, the assumption is virtually contained in it that the ions external to the group are arranged at random, and this is not actually the case. It may, however, be observed that any error due to this cause

in the intermediate formulæ will not affect the final result, since we ultimately take the limit of the virial on A_0 of its m neighbours for $m=\infty$, and this is practically equivalent to extending the group so as to include the whole of the $2N$ ions in the volume, to which case we assume that Boltzmann's theorem is applicable.

Since $P(E)$ contains the unknown constant k_m , we shall have to sum up $P(E)$ as well as $U.P(E)$, in order that, by writing $\Sigma P(E)=1$, k_m may be determined. We shall attack the summation of $P(E)$ first, because it is the more convenient for explaining the notation &c. adopted.

In carrying this out we shall make the assumption that any single term in the exponent of (11) of the type q^2/rw may be treated as a small quantity over the whole region throughout which the integration is to be effected. The conditions in which this assumption is justifiable will be best made clear by considering a simple case. Suppose that we have two ions only, a positive one A fixed at the centre of a sphere of radius R , and a negative one B , which may be situated anywhere within the sphere, the distribution being a random one except as modified by the attraction between the ions. The chance that B is situated at a distance from A between r and $r+dr$ is by Boltzmann's theorem (3) easily seen to be

$$k e^{q^2/rw} 4\pi r^2 dr / \frac{4}{3}\pi R^3. \quad . \quad . \quad . \quad (12)$$

The unknown k in this expression is given by the fact that, since B must lie within the sphere of radius R , and since also it cannot come nearer to A than a certain minimum distance of approach (say ϵ , this will depend on the sizes of A and B),

$$\int_{\epsilon}^R k e^{q^2/rw} 3r^2 dr / R^3 = 1. \quad . \quad . \quad . \quad (13)$$

What are the conditions in which the exponent q^2/rw can be treated throughout the whole region of this integration as a small quantity? At first sight it would seem that it would be necessary to suppose that ϵ must be sufficiently large to make q^2/rw small right down to the lower limit ϵ of r , but this is not really the case. For if we write r' as the smallest value of r at which $q^2/r'w$ can be considered a small quantity, by writing the integral in (13) in the form

$$\frac{3k}{R^3} \int_{\epsilon}^{r'} e^{q^2/rw} r^2 dr + \frac{3k}{R^3} \int_{r'}^R e^{q^2/rw} r^2 dr. \quad . \quad . \quad (14)$$

we can see that, so long as ϵ is not actually zero, the first of these integrals can always be made small compared with the second by sufficiently increasing the value of R . When this is the case, the error produced by treating the exponent as small throughout will be only a second order quantity. Now the problem with which we are concerned is exactly similar to the above, except that there is a large number of ions existing in a correspondingly larger volume, and an exactly similar argument will show that our assumption can always be made valid by sufficiently increasing the volume in which the ions are contained. The assumption can consequently be justified, but it is to be observed that it restricts the validity of the result for the virial to dilute concentrations of the ions. In the application to electrolytes this is equivalent to assuming that the concentration is so dilute that no appreciable association of the ions exists—at any rate as the result of the electric forces.

Returning now to the summation of (11), we shall simplify matters by choosing our units of distance and of energy so that all distances are measured in terms of $(V/2N)^{\frac{1}{3}}$ (which is the edge of a cube which on the average contains one ion) as unit, and all energies in terms of w as unit. We can then write unity for $2N/V$ and for w in (11), which then becomes

$$P(E) = k_m e^{-\sum_{p=1}^m \sum_{i=0}^{p-1} \frac{q_i q_p}{r_{ip}} - \frac{4}{3} \pi r_m^3} dv_1 dv_2 \dots dv_m. \quad (15)$$

We have now, first, keeping the signs of the ions fixed, to integrate (15) over all possible values of $v_1, v_2 \dots v_m$, and then to sum up the result for all possible arrangements of the signs.

Let $\theta_1 \phi_1 r_1, \dots, \theta_m \phi_m r_m$ be the polar coordinates of $A_1, \dots, A_m$. (15) then becomes

$$P(E) = k_m e^{-\sum_{p=1}^m \sum_{i=0}^{p-1} \frac{q_i q_p}{r_{ip}} - \frac{4}{3} \pi r_m^3} d\phi_1 \sin \theta_1 d\theta_1 r_1^2 dr_1 \dots d\phi_m \sin \theta_m d\theta_m r_m^2 dr_m \dots \quad (16)$$

This has to be integrated with respect to each θ and ϕ over the whole sphere having the corresponding r as radius. Consider the integration with respect to the θ_p and ϕ_p of a single ion A_p . Suppose that the integrations for all the ions outside A_p , *i.e.* with respect to θ_m, ϕ_m , &c., down to θ_{p+1}, ϕ_{p+1} have been already performed. It is evident that by these integrations all the terms of the form $q_p q_s / r_{ps}$, where $s > p$, will have been removed from the exponent of e in (16), and in integrating for A_p we shall be concerned only with terms

of the form $q_i q_p / r_{ip}$, where $i < p$, i. e., with the ions inside the sphere r_p . Write E_p for the mutual potential energy of A_p with respect to all the ions inside its sphere, so that

$$E_p = \frac{q_0 q_p}{r_p} + \frac{q_1 q_p}{r_{1p}} + \dots + \frac{q_{p-1} q_p}{r_{p-1,p}} = \sum_{i=0}^{p-1} \frac{q_i q_p}{r_{ip}}.$$

Then (16), so far as the integration in θ_p and ϕ_p is concerned, may be written

$$P_1(E) = \int_{\theta_p=0}^{\pi} \int_{\phi_p=0}^{2\pi} C e^{-E_p} d\phi_p \sin \theta_p d\theta_p, \quad (17)$$

where C is a factor which includes all the quantities which do not vary with θ_p and ϕ_p .

Now it is important to observe that we cannot treat E_p in (17) as a small quantity*, even though we have assumed that each individual term of it, $q_i q_p / r_{ip}$, may be treated as small; for we shall have to consider the probability of cases in which all the ions inside A_p 's sphere have the same sign, and in such cases E_p may be large if the number of ions inside is large. But it will follow from our assumption that, if $\bar{E}_p$ stands for the mean value of the mutual potential energy of A_p and the ions inside its sphere which is obtained when A_p may be situated anywhere indifferently on the surface of its sphere, then we can treat $E_p - \bar{E}_p$ as a small quantity. For E_p at any point on the surface of the sphere can only differ from its mean value over the whole surface by more than a small quantity as the result of two causes. First, there might be a very unsymmetrical arrangement (considered with regard to sign) of a large number of ions inside A_p 's sphere; for example, if all the positive ions were in one hemisphere, and all the negatives in the other, then $E_p - \bar{E}_p$ would not necessarily be small at every point of the surface. It is necessary that the number of ions should be large, for otherwise both E_p and $\bar{E}_p$ would themselves be small, and their difference still more so. But it is easily seen that as the number of ions is increased, the probability of an unsymmetrical distribution of such a type as would make $E_p - \bar{E}_p$ a large quantity, becomes smaller and smaller compared with that of a more symmetrical distribution such as would not produce the effect. Consequently, when the complete summation of (16) with respect to the positions and signs of all the ions has been effected, the total contribution to the sum due to these cases will be but a small

* The attempt to treat it as small leads to impossible results for the virial.

fraction of the whole, and therefore the error which will be produced in the whole by treating these cases as though their exponents $E_p - \bar{E}_p$ are small will be a second order quantity which may be neglected. Secondly, $E_p - \bar{E}_p$ may be large for certain positions of A_p as the result of one or more ions inside the sphere lying very close to the surface, and thus over a certain region of the integration of (17) being very close to A_p . But in accordance with our initial assumption (p. 557) a similar argument to that used above applies here also.

Treating $E_p - \bar{E}_p$ as small, we can write (17) as

$$P_1(E) = C \int_0^\pi \int_0^{2\pi} e^{-\bar{E}_p} e^{-(E_p - \bar{E}_p)} d\phi_p \sin \theta_p d\theta_p,$$

and in expanding the second exponential omit second order terms. This gives

$$\begin{aligned} P_1(E) &= C \int_0^\pi \int_0^{2\pi} e^{-\bar{E}_p} (1 - E_p + \bar{E}_p) d\phi_p \sin \theta_p d\theta_p \\ &= C e^{-\bar{E}_p} \times 4\pi, \end{aligned}$$

since the integral of $E_p d\phi_p \sin \theta_p d\theta_p$ over the surface of the sphere is by definition equal to $4\pi \bar{E}_p$. As the result of a well-known electrical theorem, $\bar{E}_p$ is equal to q_p/r_p multiplied by the total charge inside A_p 's sphere, i. e.,

$$\bar{E}_p = \frac{q_p}{r_p} (q_0 + q_1 \dots + q_{p-1}) = \frac{q_p}{r_p} \sum_{i=0}^{p-1} q_i. \quad (18)$$

We see that all the terms of (16) which before the integration involved the distances r_{ip} become changed into corresponding terms involving only the central distance r_p of the ion A_p from A_0 . The same argument now applies to the integrations for A_{p-1} , A_{p-2} , &c., down to A_1 , so that when they are carried out (16) takes the form

$$P_2(E) = k_m e^{-\left(\sum_{p=1}^m \frac{q_p}{r_p} \sum_{i=0}^{p-1} q_i\right) - \frac{4}{3} \pi r_m^3} 4\pi r_1^2 dr_1 \dots 4\pi r_m^2 dr_m.$$

For shortness, write

$$a_p = q_p \sum_{i=0}^{p-1} q_i, \quad k_1 = k_m \times (4\pi)^m, \quad \dots \quad (19)$$

so that

$$P_2(E) = k_1 e^{-\sum_{p=1}^m \frac{a_p}{r_p} - \frac{4}{3} \pi r_m^3} r_1^2 dr_1 \dots r_m^2 dr_m.$$

When we have integrated this expression over all the possible values of the r 's we shall have obtained the probability of a specified order of succession in the signs of the m nearest ions. Call this $P(m)$, as it is a function of the number of nearest ions considered. Now, when we carry out these integrations in the order $r_1 \dots r_m$ in the first integration, r_1 , being the distance from A_0 of the nearest ion, may have any value between ϵ , which is the nearest distance to which the ions can approach, and r_2 , the distance of the second nearest ion; then r_2 may be given any value between ϵ and r_3 and so on, finally r_m may have any value between ϵ and

infinity. Hence, writing $e^{-\sum_{p=1}^m a_p/r_p}$ fully, so that each factor of it may come after the first integral sign which acts upon it, we have for the integral to be evaluated

$$P(m) = k_1 \int_{r_m=\epsilon}^{\infty} e^{-\frac{4}{3}\pi r_m^3 - \frac{a_m}{r_m}} r_m^2 dr_m \int_{r_{m-1}=\epsilon}^{r_m} e^{-\frac{a_{m-1}}{r_{m-1}}} r_{m-1}^2 dr_{m-1} \dots$$

$$\int_{r_2=\epsilon}^{r_3} e^{-\frac{a_2}{r_2}} r_2^2 dr_2 \int_{r_1=\epsilon}^{r_2} e^{-\frac{a_1}{r_1}} r_1^2 dr_1. \quad (20)$$

Now so far as the integration in r_1 is concerned, we can in accordance with our assumption treat a_1/r_1 as a small quantity. But in general a_p/r_p cannot be considered a small quantity; a_p is by (19) proportional to the total charge inside A_p 's sphere, and when p is large, as has already been pointed out, this may become considerable if the ions inside have all the same sign. The successive integrations may nevertheless be carried out with a close approximation by the use of the following approximate theorem.

By integration by parts, and assuming that the term containing the lower limit is negligible, we have

$$\int_{\epsilon}^{r'} e^{-\frac{a}{r}} r^n dr = \frac{r'^{n+1}}{n+1} e^{-\frac{a}{r'}} \left\{ 1 - \frac{a}{nr'} + \frac{1}{n(n-1)} \frac{a^2}{r'^2} - \dots \right\}$$

$$= \frac{r'^{n+1}}{n+1} e^{-\frac{a}{r'} \cdot \frac{n+1}{n}}, \text{ approximately. } \dots (21)$$

In order for this approximation to hold it is not necessary that a/r , but only that a/nr , should be small. Now, in applying this theorem to the successive integrations of (20), the integrands remain of the same type throughout, and it is easy to see that the exponent of r_p , i. e., the n of (21), always increases at a greater rate than the value of a_p in the

exponential can possibly do, even in the most unfavourable case which occurs when all the ions have the same sign; consequently, α_p/nr_p is always smaller than α_1/r_1 , and the application of the theorem remains valid throughout.

Integrating successively by (21) until only the integration in r_m remains to be performed we get

$$P(m) = k_1 \int_{r_m=\epsilon}^{\infty} e^{-\frac{4}{3}\pi r_m^3} dr_m \frac{r_m^{3m-1}}{3.6.9 \dots 3(m-1)} e^{-\frac{1}{r_m} \left\{ a_1 \frac{3.6.9 \dots 3(m-1)}{2.5.8 \dots 3(m-1-\frac{1}{3})} \right.}$$

$$\left. + a_2 \frac{6.9 \dots 3(m-1)}{5.8 \dots 3(m-1-\frac{1}{3})} + a_3 \frac{9 \dots 3(m-1)}{8 \dots 3(m-1-\frac{1}{3})} \dots + a_{m-1} \frac{3(m-1)}{3(m-1-\frac{1}{3})} + a_m \right\}$$

This can be written in the form

$$P(m) = k_1 \int_{r_m=\epsilon}^{\infty} e^{-\frac{4}{3}\pi r_m^3} dr_m \frac{r_m^{3m-1}}{3^{m-1} \Gamma(m)} e^{-\frac{1}{r_m} \frac{\Gamma(m)}{\Gamma(m-\frac{1}{3})} \cdot A(m)}$$

where

$$A(m) = a_1 \frac{\Gamma(1-\frac{1}{3})}{\Gamma(1)} + a_2 \frac{\Gamma(2-\frac{1}{3})}{\Gamma(2)} + \dots + a_m \frac{\Gamma(m-\frac{1}{3})}{\Gamma(m)}$$

$$= \sum_{p=1}^m a_p \frac{\Gamma(p-\frac{1}{3})}{\Gamma(p)}.$$

To integrate it, substitute $x = \frac{4}{3}\pi r_m^3$ and write

$$\alpha = \left(\frac{4\pi}{3}\right)^{\frac{1}{3}} A(m), \quad \beta = \frac{\Gamma(m)}{\Gamma(m-\frac{1}{3})} \alpha \quad . \quad . \quad . \quad (22)$$

and $k_m = (4\pi)^{-m} k_1$ [v. (19)].

Then, writing zero instead of the negligible ϵ for the lower limit, we get

$$P(m) = \frac{k_m}{\Gamma(m)} \int_0^{\infty} x^{m-1} e^{-x-\beta x^{-\frac{1}{3}}} dx \quad . \quad . \quad . \quad (23)$$

Expanding the exponential $e^{-\beta x^{-\frac{1}{3}}}$ in series, we get

$$P(m) = \frac{k_m}{\Gamma(m)} \int_0^{\infty} e^{-x} \left(x^{m-1} - \beta x^{m-1-\frac{1}{3}} + \frac{\beta^2}{2!} x^{m-1-\frac{2}{3}} \dots \right) dx$$

$$= \frac{k_m}{\Gamma(m)} \left\{ \Gamma(m) - \beta \Gamma(m-\frac{1}{3}) + \frac{\beta^2}{2!} \Gamma(m-\frac{2}{3}) \dots \right\},$$

and on substituting the value of β given in (22) this becomes

$$P(m) = k_m \left\{ 1 - \alpha + \frac{\alpha^2}{2!} \cdot \frac{\Gamma(m)}{\Gamma(m-\frac{1}{3})} \cdot \frac{\Gamma(m-\frac{2}{3})}{\Gamma(m-\frac{1}{3})} - \frac{\alpha^3}{3!} \left(\frac{\Gamma(m)}{\Gamma(m-\frac{1}{3})} \right)^2 \cdot \frac{\Gamma(m-\frac{2}{3})}{\Gamma(m-\frac{1}{3})} \dots \right\}. \quad (24)$$

The coefficient of $\alpha^n/n!$ in this equation is

$$\left(\frac{\Gamma(m)}{\Gamma(m-\frac{1}{3})} \right)^{n-1} \cdot \frac{\Gamma(m-\frac{n}{3})}{\Gamma(m-\frac{1}{3})}.$$

When m is large the first factor of this becomes practically identical with $m^{\frac{n-1}{3}}$, and the second factor with $m^{-\frac{n-1}{3}}$, as may readily be seen by using the exponential expansion of $\Gamma(m)$. Each coefficient reduces, therefore, practically to unity, and the expression in the brackets of (24) becomes identical with the expansion of $e^{-\alpha}$. Hence,

$$P(m) = k_m e^{-\alpha} \dots \dots \dots (25)$$

We have by (22)

$$\alpha = \left(\frac{4\pi}{3} \right)^{\frac{1}{2}} \sum_{p=1}^m a_p \frac{\Gamma(p-\frac{1}{3})}{\Gamma(p)} \dots \dots (26)$$

a_p here stands for the charge on the p th nearest ion, A_p , multiplied by the total charge on the ions which are inside A_p 's sphere (see equations (18) and (19)). This is valid only for the provisional units temporarily adopted in which w and $2N/V$ were put equal to unity. We shall now revert to the ordinary units, and also understand by a_p a purely numerical factor, expressing the excess of the number of the ions of like sign to A_p over that of the ions of unlike sign, which are nearer to A_0 than A_p , A_0 being included in counting this excess. a_p will be called for shortness the "excess of like ions inside the p th," it is a fixed quantity for a definite order of succession of the signs of the ions.

Under these conditions (26) becomes

$$\alpha = \left(\frac{4\pi}{3} \cdot \frac{2N}{V} \right)^{\frac{1}{2}} \frac{q^2}{w} \sum_{p=1}^m a_p \frac{\Gamma(p-\frac{1}{3})}{\Gamma(p)}$$

(that q^2/w and $2N/V$ come in as they do is evident from the dimensions). $\frac{\Gamma(p-\frac{1}{3})}{\Gamma(p)}$ is a purely numerical function of p , which may be easily tabulated. We shall call it henceforward u_p . Values of u_p are shown in Table I.

Write h for $\left(\frac{4\pi}{3} \cdot \frac{2N}{V} \right)^{\frac{1}{2}} \frac{q^2}{w}$; h is a function of $2N/V$ the concentration of the ions, and it is the variable in terms of which the virial will be ultimately expressed.

With this notation (25) becomes

$$P(m) = k_m e^{-h \sum_{p=1}^m a_p u_p} \dots \dots \dots (27)$$

TABLE I.

$p.$	$u_p.$	$p.$	$u_p.$
1.....	1·345120	9.....	0·493155
2.....	0·902746	10.....	·474890
3.....	·752289	11.....	·459060
4.....	·668701	12.....	·445150
5.....	·612976	13.....	·432784
6.....	·572111	14.....	·421687
7.....	·540327	15.....	·411647
8.....	·514597	16.....	·402500
		17.....	·394114

We have now reduced the problem to such a form that the probability of a given order of succession of the signs of the m nearest ions, an order which may be specified by showing a particular arrangement of the symbols + and - in a row, is given by (27). Thus an arrangement of the nearest ions in which the sign of the p th nearest ion is given by the following scheme will have its probability given by (28).

$$\begin{array}{c} A_0 \\ + \end{array} \left| \begin{array}{cccccccccccccccccc} A_1 & A_2 & A_3 & A_4 & A_5 & A_6 & A_7 & A_8 & A_9 & A_{10} & A_{11} & A_{12} & A_{13} & A_{14} & A_{15} \\ + & - & + & - & - & - & + & + & + & + & - & + & - & - & - \end{array} \right.$$

$$P(m) = k_m e^{-h(u_1 - 2u_2 + u_3 - 2u_4 - u_5 - 0 - u_7 + 0 + u_9 + 2u_{10} - 3u_{11} + 2u_{12} - 3u_{13} - 2u_{14} - u_{15})}. \quad (28)$$

The coefficient of u_p in (28), being the excess of like ions inside the p th, is easily written down for each ion by inspection.

The probability $P(S)$ of the arrangement S , which is characterized by the ions being arranged + and - in regular order, is given by (29).

$$\begin{array}{c} A_0 \\ + \end{array} \left| \begin{array}{cccccccccccccccccc} A_1 & A_2 & A_3 & A_4 & A_5 & A_6 & A_7 & A_8 & A_9 & A_{10} & A_{11} & A_{12} & A_{13} & A_{14} & A_{15} \\ - & + & - & + & - & + & - & + & - & + & - & + & - & + & - \end{array} \right.$$

$$P(S) = k_m e^{+h(+u_1 + 0 + u_3 + 0 + u_5 + 0 + u_7 + 0 + u_9 + 0 + u_{11} + 0 + u_{13} + 0 + u_{15})}. \quad (29)$$

We shall call this the "standard" arrangement. It is also the most probable one, since each term of the exponential is positive, and it is easy to see by trial that any alteration of the order of succession of the signs will diminish its value, or at the most leave it unchanged.

Now a given arrangement may be specified completely by

stating the "positions" of either the + or the - ions in it (by the "position" is meant the number of the ion without regard to sign counting outwards from A_0 , *i. e.*, the suffix p of A_p). Thus, the first arrangement illustrated above is known when it is stated that the

1st, 2nd, 3rd, 4th, 5th, 6th, 7th, 8th, nearest - ions are respectively the

2nd, 4th, 5th, 6th, 11th, 13th, 14th, 15th, nearest ions to A_0 , *i. e.*, have the positions 2, 4, 5, &c. The probability of a given arrangement must consequently be expressible as a function of the positions of either of the + or of the - ions in it. We shall take the central ion A_0 as being + in all cases, and specify the arrangement by the positions of the - ions, and transform (27) so that the probability of the arrangement is given in terms of these.

Let n be the number of - ions in the arrangement of the m nearest ions to A_0 , and let the positions of the

1st, 2nd, 3rd, ... i th, ... n th, nearest - ions be respectively $p_1, p_2, p_3, \dots p_i, \dots p_n$.

Then $P(m)$ may be written as $P(p_1, p_2, p_3, \dots p_i, \dots p_n)$, and $P(S)$ as $P(1, 3, 5, \dots 2n-1)$.

Now we can transform the given arrangement into the standard one by transferring in succession each - ion from its position $p_1, p_2, \dots p_n$, to its standard position 1, 3, ... $2n-1$. By carrying out these transferences in a suitable order it can always be arranged that the order of succession of the - ions is not affected at any stage of the process. Thus the order of succession of the i th - ion will not be changed by the transference (*i. e.*, it will still remain the i th - ion) if all the ions between p_i and $2i-1$, including that at $2i-1$, are +. If this condition holds, then the transference of this ion can be effected without changing its order, and when this is done there will necessarily be some other - ion for which the same condition holds, and so on until all the transferences have been effected.

Suppose that the condition referred to above holds for the i th - ion, which we shall call B_i , then we shall consider the transference of B_i from p_i to $2i-1$ as being made as follows. We first interchange B_i at p_i and the + ion next to it, and we then repeat this process until B_i has arrived at the position $2i-1$. Let p be the position of B_i at any stage of the transference, and $p+1$ that of the adjacent + ion with which it is to be interchanged. We can state in terms of p and i the values of the coefficients a_p and a_{p+1} of the terms which

refer to these two ions in the expression (27) for the probability of the arrangement, as is done in the following table:—

Ions.....	Before interchange.		After.	
	$A_p(=B_i)$	A_{p+1}	A_p	$A_{p+1}(=B_i)$
Position of ions.....	p	$p+1$	p	$p+1$
Sign	—	+	+	—
Number of ions "inside" (including A_0).....	p	$p+1$	p	$p+1$
Number of — ions "inside"	$i-1$	i	$i-1$	$i-1$
" + " "	$p-i+1$	$p-i+1$	$p-i+1$	$p-i+2$
"Excess" of like ions "in- side" = coef. a_p or a_{p+1} .	$-(p-2i+2)$	$+(p-2i+1)$	$+(p-2i+2)$	$-(p-2i+3)$

Now interchange the two ions B_i and A_{p+1} , and we get the values for a_p and a_{p+1} , shown in the last two columns. It is easily seen that this interchange will not affect any of the coefficients a other than these two in the expression for the probability, so that we can include them all in a single constant C , for the purposes of the present argument, and write before the interchange

$$P(p_1 \dots p \dots p_n) = Ce^{-h[-(p-2i+2)u_p + (p-2i+1)u_{p+1}]},$$

and after it

$$P(p_1 \dots p+1 \dots p_n) = Ce^{-h[+(p-2i+2)u_p - (p-2i+3)u_{p+1}]}.$$

The relative probability of these two arrangements is given by

$$\frac{P(p_1 \dots p+1 \dots p_n)}{P(p_1 \dots p \dots p_n)} = e^{-2h(p-2i+2)(u_p - u_{p+1})}. \quad (30)$$

Since

$$\begin{aligned} u_p - u_{p+1} &= \frac{\Gamma(p - \frac{1}{3})}{\Gamma(p)} - \frac{p - \frac{1}{3}}{p} \frac{\Gamma(p - \frac{1}{3})}{\Gamma(p)} \\ &= \frac{1}{3p} u_p \end{aligned}$$

equation (30) may be written

$$\frac{P(p_1 \dots p+1 \dots p_n)}{P(p_1 \dots p \dots p_n)} = e^{-\frac{2}{3}h \frac{p-2i+2}{p} u_p}.$$

If p_i is greater than $2i-1$, put down the values which this

expression takes up in succession as p is given the values from $2i-1$ to p_i-1 inclusive, and multiply all the equations together. On the one side all the intermediate P 's except the first and the last cancel out, and on the other side the exponents of e all add together, giving

$$\frac{P(p_1 \dots p_i \dots p_n)}{P(p_1 \dots 2i-1 \dots p_n)} = e^{-\frac{2}{3}h \sum_{p=2i-1}^{p_i-1} \frac{p-2i+2}{p} u_p} \dots \quad (31)$$

If p_i is less than $2i-1$, the transformation is effected by giving p all values from p_i to $2i-2$, and we get an expression which may also be represented by (31) if we note that a general property of Σ considered as the sign of a summation of a function of the natural numbers n between limits which are both included in the summation, is,

$$\sum_{n=n_1}^{n_2-1} = - \sum_{n=n_2}^{n_1-1} . \quad . \quad . \quad . \quad . \quad (32)$$

(31) represents a function of p_i and i , which can be calculated without difficulty when the value of the independent variable h is given. We shall represent this function by $e_i(p_i)$, or more generally, considering it as a function of the natural numbers p , the nature of the function depending on the natural number i , as $e_i(p)$, where

$$e_i(p) = e^{-\frac{2}{3}h \sum_{p=2i-1}^{p-1} \frac{p-2i+2}{p} u_p} \quad . \quad . \quad . \quad (33)$$

Values of $e_i(p)$ for different values of p and i are given in Table II. for an assumed value of $h=0.3$. The meaning

TABLE II. of $e_i(p)$ [$h=.3$].

[illegible]

of the numbers can be explained as follows:—Consider a particular value, say $e_3(p)$ at $p=8$, or $e_3(8)$. Take a large number of instantaneous views of the central ion A_0 and its n nearest neighbours. Pick out all those views in which there are the same number n of $-$ ions present; of these pick out all the sets of views in which the 1st and 2nd, and the 4th to the n th, nearest $-$ ions are situated in any definitely fixed positions, which may be arbitrarily chosen, except for the stipulation that the 2nd $-$ ion lies inside the position 5 and the 4th outside 8. In this set there will be a certain number of views in which the 3rd $-$ ion occupies the position 8 and a certain number in which it occupies the position 5, which is the standard position for this ion. The ratio of these two numbers is $e_3(8)$ or $\cdot 89676$, and is the relative probability of the occurrence of positions 8 and 5 for the 3rd $-$ ion (the stipulation above simply meaning that both positions shall be possible ones).

If we apply the foregoing transformation to each of the n $-$ ions in succession, we see that we can write, as a complete expression for the probability of the arrangement in which the $-$ ions have the positions $p_1, \dots p_n$, relative to that in which they have the standard positions,

$$\frac{P(p_1 \dots p_i \dots p_n)}{P(1, 3, \dots 2n-1)} = e_1(p_1) \dots e_i(p_i) \dots e_n(p_n) \quad . \quad . \quad (34)$$

where the functions $e_i(p_i)$ are given by (33). The relative probability of the arrangement, as it will be called (the words “to the standard arrangement” being understood), is expressed by this equation completely in terms of the positions of the $-$ ions.

Next consider the relative probability of an arrangement in which the position of B_1 , the nearest $-$ ion, is unspecified, while all the other $-$ ions are in definite positions $p_2, \dots p_n$. By considering instantaneous views we see that it may be obtained by giving to (34) the different values which it takes up in succession for each possible position p_1 of B_1 , *i. e.*, for the values of p_1 from 1 to p_2-1 inclusive, and summing the results. Since $e_2(p_2) \dots e_n(p_n)$ are constant in this summation they may be taken outside the Σ , and, writing them in the reverse order to (34), we get for the relative probability

$$e_n(p_n) \dots e_2(p_2) \sum_{p_1=1}^{p_2-1} e_1(p_1) \quad . \quad . \quad . \quad (35)$$

The relative probability of an arrangement in which not only the position of B_1 , but also that of B_2 , the second

nearest — ion, is unspecified, may now be obtained by summing the different values which (35) takes up for each possible position p_2 of B_2 , *i. e.*, for the values of p_2 from 2 to $p_3 - 1$ inclusive ; this gives

$$e_n(p_n) \dots e_2(p_3) \sum_{p_2=2}^{p_3-1} e_2(p_2) \sum_{p_1=1}^{p_2-1} e_1(p_1).$$

This process is evidently general. Carrying it out for all the ions, we have for the relative probability of an arrangement of m nearest ions containing $n -$ ions, in which the positions of the $n -$ ions are all unspecified—we shall call this $f_n(m)$ —

$$f_n(m) = \sum_{p_n=n}^m e_n(p_n) \sum_{p_{n-1}=n-1}^{p_n-1} e_{n-1}(p_{n-1}) \dots \sum_{p_2=2}^{p_3-1} e_2(p_2) \sum_{p_1=1}^{p_2-1} e_1(p_1) \quad (36)$$

The quantity $f_n(m)$ may be considered a function of the natural number m , the nature of the function depending on the natural number n . (It is of course also a function of the independent variable h .) It may be tabulated for different values of m and n , by employing on the numbers for $e_i(p)$ of Table II. a process of successive additions similar to

TABLE III. of $f_n(m)$ [$h=3$].

m .	$f_1(m)$.	$f_2(m)$.	$f_3(m)$.	$f_4(m)$.	$f_5(m)$.	$f_6(m)$.	$f_7(m)$.	$f_8(m)$.
1 ...	1'000							
2 ...	1'76275	1'000						
3 ...	2'3995	2'76275	·97100					
4 ...	2'9473	5'0449	3'7338	·90411				
5 ...	3'4275	7'6667	8'7787	4'5474	·7962			
6 ...	3'8515	10'4995	16'2597	13'3261	5'106	·679		
7 ...	4'2295	13'4489	26'1216	29'586	18'228	5'378	·5621	
8 ...	4'5689	16'4472	38'182	55'308	47'824	22'950	5'372	·4527
9 ...	4'8751	19'4455	52'191	91'950	103'132	70'253	26'981	5'126
10 ...		22'4084	67'871	140'416	194'079	173'385	95'339	29'863
11 ...			84'939	201'093	330'349	367'464	267'28	120'867
12 ...				273'926	520'68	695'064	634'74	382'47
13 ...					772'37	1203'81	1329'81	1013'01
14 ...						1943'57	2525'64	2342'82
15 ...							4433'21	4868'46
16 ...								9277'46

that adopted in the formation of the ordinary arithmetical triangle. Table III. shows values of $f_n(m)$ for $h=3$. The construction of the table may be most simply explained by observing that, as follows at once from (36),

$$f_n(m) = f_n(m-1) + f_{n-1}(m-1)e_n(m).$$

By this relation each term may be obtained in succession. As an example the following numbers are abstracted from the tables:—

$$f_3(8) = f_3(7) + f_2(7) \times e_3(8)$$

or $38.182 = 26.1216 + 13.4489 \times .89676.$

Tabulation of the values of $f_n(m)$ is equivalent to determining the absolute probability of a specified arrangement of the ions under a certain restriction, namely, that the m nearest ions contain n — ions. This last restriction might obviously be removed by an additional summation, but it will be more convenient for the calculation of the arithmetical value of the virial to work out the results in terms of $f_n(m)$.

When we confine our attention to those views of the m nearest ions in which n — ions are contained, the absolute probability of an arrangement in which the positions of the n — ions are unspecified may evidently be taken as 1, the relative probability is as we have seen $f_n(m)$, therefore, since the relative probability of an arrangement specified by the positions $p_1 \dots p_n$ of the — ions is given by $e_1(p_1) \dots e_n(p_n)$, it follows that the absolute probability of this arrangement is

$$P(m) = \frac{e_1(p_1) \dots e_n(p_n)}{f_n(m)}, \dots \dots (37)$$

(37) may now be used in place of the expression (27)

$$P(m) = k_m e^{-h \sum_{p=1}^m a_p u_p},$$

for the same probability; it differs from (27) in that all the quantities in it are numerically determinate, whereas (27) contains the unknown k_m . We have thus solved the first part of our problem, since we can now by (37) and (27) eliminate k_m from our expressions whenever we please.

We can now return to the original problem of determining the average virial on A_0 of the m nearest ions. We have first to integrate expression UP(E), or by (10) and (16) its equivalent

$$\sum_{\nu=1}^m \frac{q_0 q_\nu}{r_\nu} k_m e^{-h \sum_{p=1}^m \sum_{i=0}^{p-1} \frac{q_i q_p}{r_{ip}}} - \frac{4}{3} \pi r_m^3 \dots d\phi_1 \sin \theta_1 d\theta_1 r_1^2 dr_1 \dots \dots \dots d\phi_m \sin \theta_m d\theta_m r_m^2 dr_m,$$

over all possible values of ϕ , θ , and r . The integrations are carried out exactly as on pp. 558 to 564, and give

$$\int \text{UP(E)} = \sum_{\nu=1}^m \pm w h u_\nu \cdot k_m e^{-h \sum_{p=1}^m a_p u_p} \dots \dots (38)$$

where h , u_p , and a_p are the quantities defined on p. 563, and

$$v_p = \frac{\Gamma(p - \frac{1}{3})}{\Gamma(p)} \times \frac{\Gamma(\nu)}{\Gamma(\nu - \frac{1}{3})} \cdot \frac{\Gamma(\nu - \frac{2}{3})}{\Gamma(\nu - \frac{1}{3})} \text{ when } p < \nu, \text{ and} \\ = \frac{\Gamma(p - \frac{2}{3})}{\Gamma(p - \frac{1}{3})} \text{ when } p > \nu. \quad (39)$$

The $\pm$ in (38) is meant to indicate that the sign of the term in the summation in ν is to be taken $+$ or $-$ according as the ν th ion is $+$ or $-$.

(38) when summed over all the possible orders of succession in the signs of the ions (we will call this sum $\Sigma \int UP(E)$) will give the total average virial on A_0 of the m nearest ions. $\int UP(E)$ is the term contributed to this sum corresponding to a particular arrangement of the signs of the ions specified by the values of the a 's. We will call it for shortness the "virial contribution" of the arrangement.

In order to obtain $\Sigma \int UP(E)$ we theoretically require to proceed as follows. We must first of all transpose (38) so that the virial contribution is specified in terms of the positions of the $-$ ions in the arrangement. Then, taking a single term of (38), say that corresponding to the ν th ion, we must sum it up for all the cases in which the ν th ion is $+$, *i.e.*, for all the cases in which the 1st $+$ ion is the ν th, the 2nd the ν th, &c., and subtract the similarly obtained sum of all the cases in which the ν th ion is $-$. The total average virial on A_0 of all the m ions is then obtained by giving to ν the values from 1 to m in succession, and adding the results. The symbolical expressions from which these may be calculated for any finite number of ions may be written down without difficulty, but the work of getting arithmetical values from them is very laborious. The reason of this is that the v_p of (38) is really, as is seen from (39), a function of ν as well as of p , consequently the functions which have to be summed take up a different form for each value of ν . If v_p were only independent of ν , the arithmetical calculation would be much simpler. In order to obtain numerical values of the average virial, so that a curve showing the way in which it varies with the concentration of the ions can be plotted, I have contented myself with a calculation from an approximation to (38) for the virial contribution, which is explained and justified in the following paragraph.

Consider the meaning of the expression for the virial contribution in more detail. $+whu_p$ represents the mean

value over all distances of q^2/r_v , or of the virial on A_0 of the v th nearest ion (assumed of positive sign), on a purely random distribution of the ions. This can readily be proved by direct integration, or it follows at once from (38) since the exponential there reduces to 1 when the distribution is a

random one. Hence $\sum_{v=1}^m \pm whu_v$ is the mean virial of a par-

ticular arrangement on a random distribution. The virial contribution of a particular arrangement on a random dis-

tribution would be $\sum_{v=1}^m \pm whu_v \times \frac{1}{2^m}$, since $1/2^m$ is the chance

of this arrangement when the m nearest ions only are considered. Now in the distribution as modified by the inter-ionic forces the contribution will be different from the above for two reasons. First, the chance of the given arrangement will be different—we have seen [(27)] that this is

$$k_m e^{-h \sum_{p=1}^m a_p u_p},$$

and, secondly, the mean virial of the arrangement will not be exactly the same as it would be on a random distribution, because the inter-ionic forces, as well as affecting the chance of a given arrangement of signs, will also affect the mean distances of the ions. We shall here, however, neglecting the second of these effects in comparison with the first, assume that the

mean virial of the arrangement is still given by $\sum_{v=1}^m \pm whu_v$ in

the modified distribution. We shall then be able to write for the virial contribution of the arrangement as an approximation to (38)

$$\int \text{UP}(E) = \sum_{v=1}^m \pm whu_v \times k_m e^{-h \sum_{p=1}^m a_p u_p}. \quad (40)$$

It is possible to show that the approximation is valid when h is sufficiently small. (40) differs from (38) only in that v_p is replaced by u_p . It follows from the expression for v_p that when v is moderately large (say greater than 10) v_p becomes practically identical with u_p . The virial contribution of all except the first few nearest ions will, therefore, be accurately represented by (40), and it is only in respect to the average virials of these first few ions that any error will be introduced by its use. Now it can be shown that as h becomes smaller the average virial of these first few ions becomes a smaller and smaller fraction of the whole, and the

error produced by substituting u_p for v_p will become smaller and smaller as h diminishes.

Using the approximation (40) for the virial contribution of the arrangement, we can adopt a simpler method of summation than that previously described, since the exponential, being now independent of ν , can be taken outside the Σ , thus

$$\int UP(E) = wh \left(\sum_{\nu=1}^m \pm u_{\nu} \right) \times k_m e^{-h \sum_{p=1}^m a_p u_p}.$$

If the arrangement contains n — ions, which have the positions $p_1 \dots p_n$, then

$$\sum_{\nu=1}^m \pm u_{\nu} = u_1 + u_2 \dots - u_{p_1} + u_{p_1+1} \dots - u_{p_2} + \&c. \quad (41)$$

Let $S(m) = -u_1 + u_2 - u_3 + u_4 - \dots$ to m terms. . (42)

$whS(m)$ is the mean virial on A_0 of the standard arrangement of m alternate — and + ions. From (41) and (42) we get

$$\begin{aligned} \sum_{\nu=1}^m \pm u_{\nu} &= S(m) + 2[(u_1 - u_{p_1}) + (u_3 - u_{p_2}) + (u_5 - u_{p_3}) + \&c.] \\ &= S(m) + 2 \sum_{i=1}^n u_i(p_i), \end{aligned}$$

where $u_i(p_i)$ is written for shortness for $u_{2i-1} - u_{p_i}$. The values of $u_i(p_i)$ may easily be calculated as desired from the table of u_p on p. 564. For example

$$u_3(8) = u_5 - u_8 = 0.61298 - 0.51460 = 0.09838.$$

We have also, by (37) and (27)

$$k_m e^{-h \sum_{p=1}^m a_p u_p} = \frac{e_1(p_1) \dots e_n(p_n)}{f_n(m)},$$

consequently

$$\int UP(E) = wh \left[S(m) + 2 \sum_{i=1}^n u_i(p_i) \right] \times \frac{e_1(p_1) \dots e_n(p_n)}{f_n(m)}.$$

All the possible orders of succession in the signs will be obtained by summing with respect to p_1 from 1 to p_2-1 inclusive, then with respect to p_2 from 2 to p_3-1 , and so on, finally with respect to p_n from n to m . Now in these summations $S(m)$ is a constant, and can be taken outside the Σ 's. Also each $u_i(p_i)$ is constant until that summation which applies to p_i has been reached. Taking these facts

into account, and putting the Σ signs in their proper places so that each acts only on what comes to its right, we get for the complete average virial on A_0 , $\overline{U_n(m)}$, of all arrangements of the m nearest ions, which contain among them $n -$ ions,

$$\overline{U_n(m)} = \frac{wh}{f_n(m)} \left[S(m) \sum_{p_n=n}^m e_n(p_n) \dots \sum_{p_1=1}^{p_2-1} e_1(p_1) \right. \\ \left. + 2 \sum_{i=1}^n \left\{ \sum_{p_n=n}^n e_n(p_n) \dots \sum_{p_{i+1}=i+1}^{p_{i+2}-1} e_{i+1}(p_{i+1}) \sum_{p_i=i}^{p_{i+1}-1} e_i(p_i) u_i(p_i) \sum_{p_{i-1}=i-1}^{p_i-1} e_{i-1}(p_{i-1}) \dots \sum_{p_1=1}^{p_2-1} e_1(p_1) \right\} \right].$$

Now the first of the terms in the brackets is, by (36), $S(m) \times f_n(m)$, and denoting the remaining term by $2g_n(m)$, we have

$$\overline{U_n(m)} = wh \left[S(m) + 2 \frac{g_n(m)}{f_n(m)} \right]. \quad (43)$$

Using the notation of (36) for $g_n(m)$ also, we can write it

$$g_n(m) = \sum_{i=1}^n \left\{ \sum_{p_n=n}^m e_n(p_n) \dots \sum_{p_i=i}^{p_{i+1}-1} e_i(p_i) u_i(p_i) f_{i-1}(p_i-1) \right\},$$

and we see from this, by putting $i=1, 2, 3, \dots n$, in succession in it, that

$$g_n(m) =$$

$$\sum_{p_n=n}^m e_n(p_n) \left[u_n(p_n) f_{n-1}(p_n-1) + \sum_{p_{n-1}=n-1}^{p_n-1} e_{n-1}(p_{n-1}) \left\{ u_{n-1}(p_{n-1}) f_{n-2}(p_{n-1}-1) + \Sigma \right. \right. \\ \left. \left. \dots + \sum_{p_2=2}^{p_3-1} e_2(p_2) [u_2(p_2) f_1(p_2-1) + \sum_{p_1=1}^{p_2-1} e_1(p_1) u_1(p_1)] \dots \right\} \right], \quad (44)$$

in which each Σ applies to everything that comes after it. From this equation the numerical value of $g_n(m)$ for any finite values of n and m may be calculated from the tables of $e_n(m)$ and $f_n(m)$ previously given, by successive operations of a similar type to those used in forming the table for $f_n(m)$. Table IV. gives a series of values of $g_n(m)$ for $h=3$. The construction of the table may be most simply explained by noting that (44) shows that the values must satisfy the following difference equation:—

$$g_n(m) = g_n(m-1) + e_n(m) \{ g_{n-1}(m-1) + u_n(m) f_{n-1}(m-1) \}.$$

For example (see Tables II. & III., and for $u_3(8)$ p. 573)

$$g_3(8) = g_3(7) + e_3(8) \{ g_2(7) + u_3(8) f_2(7) \},$$

$$\text{or } 14.803 = 8.1149 + .89676 \{ 6.1352 + .09838 \times 13.4489 \}.$$

TABLE IV. $g_n(m)$ [$h=.3$].

m .	$g_1(m)$.	$g_2(m)$.	$g_3(m)$.	$g_4(m)$.	$g_5(m)$.	$g_6(m)$.	$g_7(m)$.	$g_8(m)$.
0 ...								
1 ...	0							
2 ...	+34428	- 15046						
3 ...	+ 72749	+ 19382	- 27560					
4 ...	1 10297	+ 1 07649	- 23572	- 37267				
5 ...	1 4589	2 4229	+ 84078	- 86737	- 42358			
6 ...	1 7904	4 1390	+ 3 5107	- 30557	- 1 5860	- 43797		
7 ...	2 0981	6 1352	8 1149	+ 3 2051	- 2 5060	- 2 2796	- 42305	
8 ...	2 3830	8 3352	14 803	+ 11 8576	+ 0645	- 5 6713	- 2 8553	- 38729
9 ...	2 6466	10 6760	23 581	27 793	+ 11 922	- 7 2200	- 9 4998	- 3 2521
10 ...		13 1065	34 355	52 863	41 073	+ 3 0694	- 19 404	- 13 546
11 ...			46 966	88 508	97 022	+ 44 142	- 20 879	- 36 382
12 ...				135 71	189 93	144 916	+ 18 718	- 65 580
13 ...					329 82	343 86	+ 163 64	- 60 309
14 ...						687 39	518 48	+ 89 981
15 ...							1233 45	+ 608 46
16 ...								1875 50

Now from equation (43), when tables of $f_n(m)$ and $g_n(m)$ have been calculated for a given value of h , we can determine for that value of h the average virial on A_0 for all the possible arrangements of any finite number m of nearest ions which contain among them a given number n of negative ions. The result is of course a function of m, n , and h . The complete average virial of all the ions on A_0 would be theoretically obtained by proceeding to the limits in which $m=\infty$, and n is unspecified. (43) would then become a function of h only, of the form

$$\bar{U} = wh\phi(h),$$

where $\phi(h)$ is the value of the expression in the brackets of (43) when $m=\infty$, and n is unspecified. To satisfy the conditions with regard to n theoretically requires an additional summation over all the possible values of n , but practically the necessity for this is removed by observing that as m becomes infinite, n must tend indefinitely towards the value $m/2$, for the probability of arrangements in which this condition does not hold becomes indefinitely small. I have not been able to find an accurate algebraical expression* for the limit of (43) when $m=\infty$, but an approximate arithmetical value can be obtained if we take n differing from $m/2$ by any finite number, and determine the virial for successively increasing values of m and plot the results on a

* It may be shown that, as an approximation, and when h is very small,

$$\bar{U} = -wh \times \sqrt{\frac{2}{\pi}h}.$$

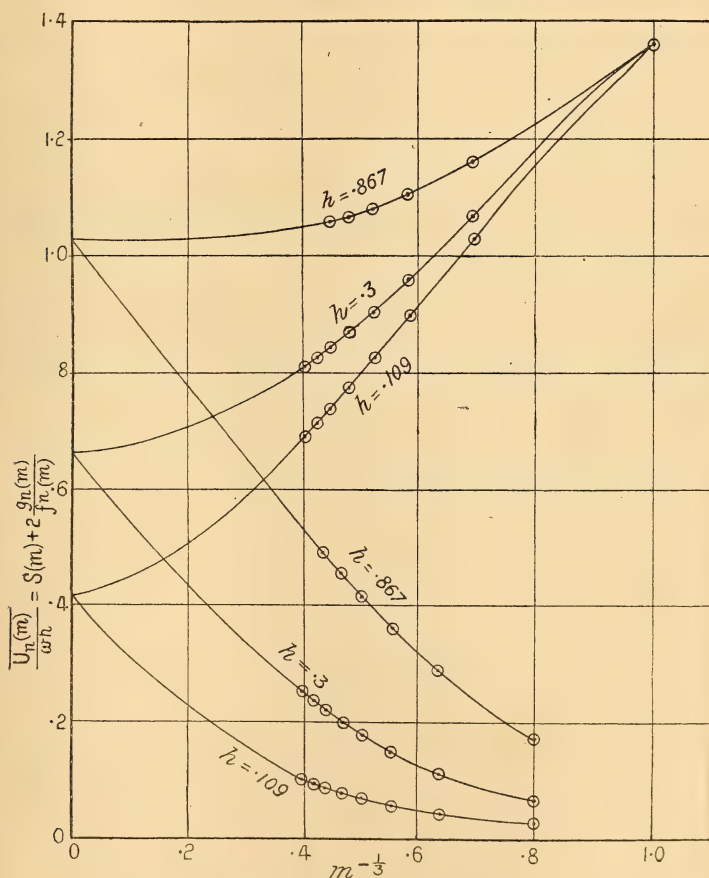
curve; the limit is then obtained by extrapolation to $m = \infty$. A practical difficulty comes in due to the fact that the rate at which the curves converge to the limit is extremely slow, but by considering the curves corresponding to two specially chosen arrangements, it is nevertheless possible to obtain a fair approximation to the limit at $m = \infty$. If we plot the curves of $\overline{U}_n(m)$, taking cases in which m is always equal to $2n$, we are confining our attention to arrangements in which the numbers of $+$ and $-$ ions surrounding the central ion A_0 are always equal. The virial for any finite number of nearest ions will then always be less than the limiting value for an infinite number, since the $m+1$ th ion, which is not included, always tends to be a $-$ one. Again, if we extrapolate from cases in which $m = 2n - 1$, we confine our attention to arrangements in which there are equal numbers of $+$ and $-$ ions when A_0 is included, *i. e.*, to arrangements which possess no total charge. In this case it follows from (27) that the ions external to the arrangement will be distributed at random with respect to A_0 , and will on the average have no virial on it. The virial of these arrangements will always be in excess of the limit.

The following table shows the values of $\overline{U}_n(m)/wh$ for $h = .3$, in these two sets of cases. The values of $f_n(m)$ and $g_n(m)$, which correspond to them, are printed in Tables III. & IV. in thicker type. The first set of values shows a continual increase, and the second a continual decrease with m . In the diagram the values are plotted against $m^{-\frac{1}{2}}$ as abscissæ.

TABLE V.

$n.$	$m.$	$S(m).$	$2 \frac{g_n(m)}{f_n(m)}.$	$\overline{U}_n(m)/wh.$
1	2	-.45137	.39061	-.06076
2	4	-.53496	.42677	-.10819
3	6	-.57583	.43182	-.14401
4	8	-.60156	.42879	-.17277
5	10	-.61982	.42326	-.19656
6	12	-.63373	.41699	-.21674
7	14	-.64483	.41057	-.23426
8	16	-.65398	.40432	-.24966
1	1	-1.35412	0	-1.35412
2	3	-1.20366	.14031	-1.06336
3	5	-1.14794	.19155	-.095639
4	7	-1.11615	.21666	-.89949
5	9	-1.09471	.23120	-.86351
6	11	-1.07888	.24023	-.83865
7	13	-1.06652	.24611	-.82041
8	15	-1.05648	.24996	-.80652

The extrapolation of these curves to the axis is certainly a rather violent one, but it may be done with some confidence by observing the following points:—(1) the first curve must be everywhere below the limit and the second one everywhere above it; (2) the two curves must extrapolate to the same point on the axis; (3) from the fact that the virial of the ions external to the second arrangement is zero, it may be inferred that the second curve for large values of m approaches the limit much more closely than the first one, and that it probably tends to become parallel to the axis as $m^{-\frac{1}{3}}$ becomes



zero. Taking these facts into account, I estimate the limit (see curve) as $\phi(h) = -0.66$. This gives for the average

virial on A_0 of all the remaining ions in the volume the value

$$\bar{U} = -wh \times 0.66 = -0.198 w, \quad \text{for } h = 0.3.$$

The figure also contains the curves which correspond to two other values of h , and in the following table the values of $\phi(h)$ obtained are gathered together, in order to show the course of the function.

$h.$	$\phi(h).$
0	0
0.109	-0.42
0.3	-0.66
0.867*	-1.03

* This value of h is so large that the expression for the virial obtained in this paper would no longer be valid; $\phi(h)$ was calculated only because it was of interest to trace the course of the function.

As h increases from 0, $\phi(h)$ increases very rapidly at first, afterwards more slowly, and it tends to become practically constant as h continues to increase. It is easy to show that when $h = \infty$ $\phi(h)$ has the limiting value of $-u_1$ or -1.354 .

The average virial $\bar{E}$ of all the ions is obtained by multiplying $\bar{U}$ by N , the number of + or of - ions in the volume V . We can therefore express it finally as

$$\bar{E} = N\bar{U} = Nwh\phi(h),$$

where $w (= RT/\nu, \text{ eq. 2})$ is the most probable kinetic energy of an ion,

$$h = \left(\frac{4\pi}{3} \cdot \frac{2N}{V} \right)^{\frac{1}{3}} \frac{q^2}{w}$$

(q being the ionic charge), and $\phi(h)$ is a function of h , the course of which is shown in the preceding table †. In a subsequent paper I hope to deal with some of the applications of this result to the osmotic pressure of electrolytes.

† This result is only strictly applicable when h is small.

L. *The Influence of the Contact Difference of Potential between the Plates emitting and receiving Electrons liberated by Ultra-violet Light on the Measurement of the Velocities of these Electrons.* By KARL T. COMPTON, M.S., Porter Ogden Jacobus Fellow, Princeton University *.

[Plate IX.]

1. **INTRODUCTION.**—It is well known that when two metallic plates are connected to the terminals of any instrument measuring difference of potential, the actual field between the plates is measured by the reading of the instrument plus or minus a certain contact difference of potential which depends on the materials of the plates and the conditions of their surfaces. Thus one would expect that an electron, moving between the plates, would be acted on by a force due to the contact difference of potential as well as by the force due to the difference of potential indicated by the voltmeter or electrometer. The contact difference of potential between metals may be as large as one volt. The measurements of the velocities of the electrons liberated by ultra-violet light have shown that they possess sufficient initial kinetic energy to carry them against fields of from zero to six volts, approximately. Thus the contact difference of potential between the plates may be a very large percentage of the total potential difference, and yet its influence seems never to have been taken into account. It is the purpose of this paper to present evidence proving that the contact difference of potential must be taken into account when making velocity measurements in the photo-electric effect, and then to show how this fact modifies some of the results which have been obtained in making measurements of the electron velocities.

2. *Apparatus* (fig. 1).—Light from an iron arc passes through a diaphragm *d* and a quartz window A; then through suitably lined holes in the mica shield F, the brass cylindrical box B, the perforated metallic box C, and strikes the polished aluminium plate D. It is thence reflected out again through holes in C, B, and F and through the glass window E. The parts B, C, and D are insulated from each other, and the electrical connexions are shown in fig. 2.

B is 5 cm. in diameter and 1 cm. high. The hole through which the light enters B is 1 mm. in diameter, and the hole in the mica screen above it is just enough smaller to prevent

* Communicated by Prof. O. W. Richardson.

any portion of the ultra-violet light from striking B. The exit-hole in B is 3 mm. in diameter. By looking in through the window E and adjusting the levelling-screws shown in the figure, these holes may all be put in the line, $\overline{abc}$, of the

Fig. 1.

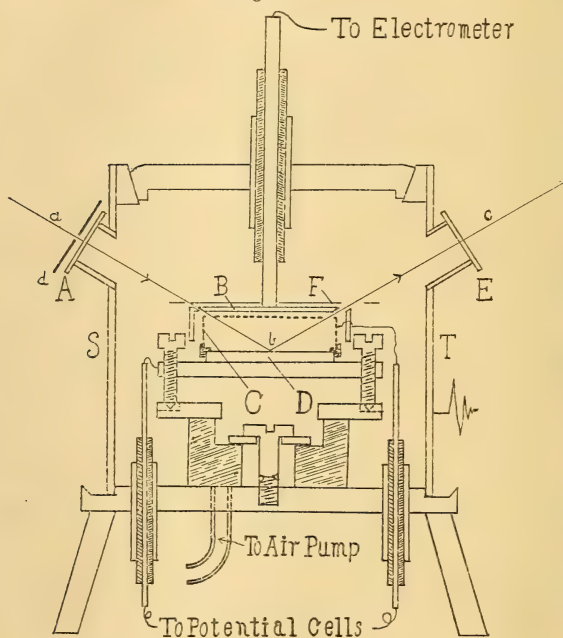
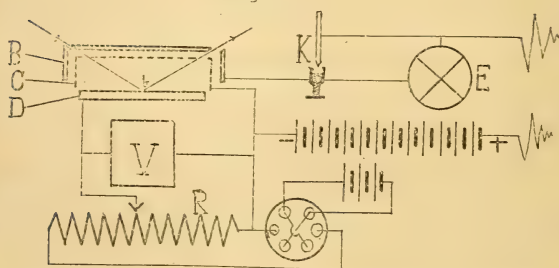


Fig. 2.



light. Several perforated metallic boxes C were prepared. One set, as nearly similar to each other in dimensions as could be made, was prepared by simultaneously drilling holes as near together as possible in the foils of aluminium, zinc, lead, iron, and copper. One was also made of platinum foil,

but in this case the foil was much thinner than in the others. Then there was one of platinum wire gauze and one of nickel wire gauze, but these were not of the same size wire nor of equal mesh. The whole apparatus was enclosed in an air-tight cylindrical brass box $\overline{ST}$ which was connected with a mercury pump and a tube of coconut charcoal.

The electrons leave at b on the plate D. The relative number reaching the perforated box C is regulated by varying the potential between C and D by means of the sliding resistance R. The voltmeter V shows this difference of potential. The electrons which reach C are caught by the strong field between C and B and are swept on to the brass box B which is connected to a Dolazalek electrometer with a sensibility of 420 divisions per volt. The connexions are so arranged that initially B is at zero potential in order to avoid, as far as possible, any leak of electricity from B. The perforated box C serves a triple purpose. It prevents the loss of electrons from B due to diffusely reflected light; it precludes the possibility of reflected electrons^{*}; and it enables the potential V to be kept constant while the electrometer is charging up. Finally, everything connected with the electrometer is enclosed in earthed metal casing to prevent electrostatic disturbances from external causes.

3. *Method.*—In taking the readings for the “distribution of velocity” curve, a difficulty arose from the flickering of the iron arc, which caused large variations in the intensity of the light during the time necessary to take a complete set of readings. This was overcome by the method of taking reading illustrated in Table I. Here V represents the reading of the voltmeter and A is the deflexion of the electrometer in 15 seconds. Readings were taken alternately with $V=0$ and V =whatever number of volts was desired. Then the ratio of the deflexion for $V=(?)$ to the deflexion for $V=0$ was determined and placed in the column marked R. Thus all the readings were referred to the readings with $V=0$ as a standard. In plotting, the average of a number of these ratios for a given value of V was plotted as an ordinate. The maximum average ratio obtained with any value of V was taken as unity and the other ratios plotted accordingly. Thus the ordinates are proportional to the number of electrons reaching B in a unit time. The voltmeter readings were plotted as abscissæ, being called negative when in such a direction as to hinder an electron passing from D to C. The velocity of an electron is then

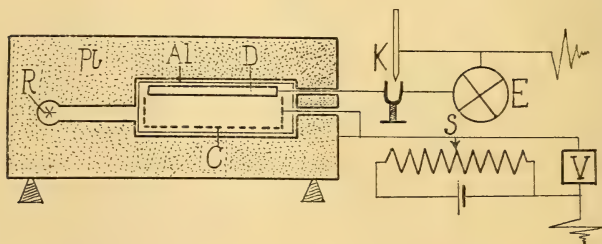
* O. v. Baeyer, *Verh. d. D. Phys. Ges.* x. p. 96 (1908).

$V = \sqrt{\frac{2Ve}{m}}$, where e and m are the charge and mass associated with an electron, and V is the largest potential against which it can reach C from D.

The general plan of procedure was to (1) polish the plate D with chalk-dust; (2) measure the contact difference of potential between D and C; (3) exhaust the apparatus, first with the mercury pump and then with coconut charcoal immersed in liquid air, and then take readings for a "distribution of velocity" curve by measuring the rate of deflexion of the electrometer for different values of V as described; (4) let air into the apparatus and again measure the contact difference of potential. The average of the two values for the contact difference of potential was the value made use of. These two readings were made since, after polishing, metals become more electronegative with time. This is especially true in the case of aluminium*. Then a perforated box C of another metal was substituted and the previous procedure repeated, keeping all other conditions in the two cases as nearly identical as possible. If there is an effective field between C and D due to the contact difference of potential between C and D, the curve obtained in the second case should differ from that in the first case by being shifted along the axis of V by an amount corresponding to the contact difference of potential between the metals used for C in the two cases.

The contact difference of potential between C and D was measured by the following method (fig. 3). C and D were

Fig. 3.



placed in the aluminium-lined cavity in a lead block. The air between C and D was ionized by radium placed at R. If the lead block and box C are earthed, an electrometer, connected with D, will charge up to a potential equal to the contact difference of potential between C and D. In this

* Winkelmann, *Handbuch der Physik*, 1st edition, vol. iii. p. 118.

work a zero method was employed. The lead box and the perforated box C were insulated from D and from the earth, and their potential so regulated by the sliding contact S that there was no deflexion of the electrometer connected with D. Then the voltmeter V gave a direct reading of the contact difference of potential between C and D.

4. *Effect of the Field between the Brass Box B and the Perforated Box C.*—Before taking up the effect of the contact difference of potential, the effect of the field which sweeps the electrons from the perforated box C to the box B will be shown. In Table I. are given the readings for curve (a) (Pl. IX. fig. 4). In this case the difference of potential between C and B was 400 volts; and C was the platinum-foil box, electrolytically copper-plated. These readings are a type of those obtained for all the curves in this paper, except that in the following sections at least ten ratios were averaged to get each point on the curve.

TABLE J.

V.	A.	R.	V.	A.	R.
-2	58	.91	-4	50	.53
0	64		0	94	
-2	60	.92	-4	52	.50
0	65		0	105	
-2	90	1.00	-4	50	.48
0	90		0	104	
-2	78	.89	-4	55	.56
0	88		0	98	
-2	82	.97	-4	50	.52
0	85	.94	0	95	.52
-3	72	.92	-5	30	.34
0	78		0	88	
-3	80	.89	-5	30	.33
0	90		0	90	
-3	95	.85	-5	26	.29
0	112		0	90	
-3	90	.80	-5	24	.30
0	112		0	80	
-3	80	.84	-5	21	.30
0	95	.86	0	75	.31

This curve and others similarly taken with different potentials between C and B are shown in Pl. IX. fig. 4.

These curves show plainly that the position of the curves is a function of the difference of potential between C and B. Evidently when this perforated box is used, every addition

of 80 volts to the field between C and B shifts the curve to the left about one volt. This indicates that the perforated foil is not a perfect shield, and that a part of the field existing on the upper side of C makes itself felt below C*. If this "stray field" explanation is correct, one would expect that if the perforations in C were larger, the amount of stray field existing on its under side would be increased. This was tested by obtaining a series of curves similar to those in fig. 4 (Pl. IX.), but using the platinum wire gauze box instead of the perforated foil box for C. In this second case the proportion of open to closed space in the box was decidedly larger than in the first case. Now it was found that the curves were shifted about 1.5 volts to the left for each 80 volts added between C and B, as against one volt to 80 in the first case. This confirms the explanation given.

Since, then, the field between C and B exerts some small effect on the under side of the perforated box C the curves which are given in the following sections are all shifted somewhat to the left of their true positions. Curves (*h*) and (*i*) and the method of finding the true positions of the curves will be explained later (section 6). It may be noted here that the curves to the right in fig. 4 (Pl. IX.) are more erect than are those to the left. This is explained simply and consistently with the view we have taken, when one remembers that the electrons which are moving most rapidly when they reach C are the most likely to strike and stick to C itself. It takes a stronger field to bend their paths so as to draw them through the perforations than to do this for the slow moving electrons. Thus, in the case of the curves to the left, practically all the electrons are drawn through the perforations in C, while farther to the right the curves indicate that a larger proportion of the high velocity electrons fail to get through. Hence the curves to the left should be less erect and should more nearly represent the true shape of the "distribution of velocity" curve. That this is true receives additional confirmation in section 7.

From these results it was evident that to compare the curves obtained when different metallic boxes were used

* This is apparently in contradiction to the results found by E. Ladenburg and K. Markau (*Phys. Zeit.* ix. p. 821, 1908), who found, with an arrangement somewhat similar to this, that, as the difference of potential above the perforated screen was increased, the curves shifted to the left until the difference of potential was 50 volts. After this they found the position of the curves to be independent of the difference of potential above the screen. They explained this result as being due entirely to the prevention of electron reflexion and not to the stray field through the perforations.

for C, it was necessary that these boxes be exactly similar in dimensions and that the field between C and B be kept constant.

5. *The Effect of Contact Difference of Potential.*—The first metals investigated were aluminium, zinc, lead, and copper. For this purpose the perforated foil boxes of these metals were successively used as C, and the curve was plotted for each one. It was noted in section 2 that the boxes of these metals were all practically similar, and thus they could be compared with each other without introducing the error entering in when the boxes are geometrically dissimilar. As a preliminary step a very large number of readings were taken and curves plotted which showed conclusively that the actual shape of the "distribution of velocity" curve is independent of the metal used as C. When once the shape of this curve had been very carefully determined, only one or two points on each curve were sufficient to completely determine it. This enabled the readings for any curve to be taken rapidly, thus lessening the change in the contact difference of potential during the experiment and permitting the two metals which were to be compared to be investigated the same day. This reduced the danger of introducing any error due to a change in the setting of the apparatus. As an additional precaution, the following procedure was adopted. Take, for instance, the perforated boxes of zinc and copper. A curve was taken using copper, then one using zinc, and again one using copper. If there was any difference in the positions of the two curves for copper, the mean of the two was taken as the correct position. In this way the curves of fig. 5 (Pl. IX.) were obtained. For all of these the difference of potential between C and B was 400 volts.

It is seen that the curves for the case of the electropositive metals lie to the left and in the order of the electropositive series. This is just what would be the case if the contact difference of potential between the aluminium plate, D and the perforated box C influences the paths of the electrons. A box C of an electropositive metal would tend to attract the negative electron more than would an electronegative metal. Thus, for the same externally applied difference of potential, many electrons would reach the electropositive box which would fall short of the electronegative box, and hence the curve for the former would lie to the left of that for the latter.

In order to test the platinum box special means had to be employed, since there was no other box of a different material

and of the same dimensions. This difficulty was overcome by obtaining the curve for platinum, then electrolytically copper-plating the box and obtaining with it the curve for copper. For convenience in this case the potential between C and B was reduced to 8 volts. Under these conditions the curves of fig. 6 (Pl. IX.) were obtained. We see, as before, that the curve for the electropositive metal falls to the left.

Table II. gives a quantitative estimate of the relation between this shift of the curves and the contact difference of potential between the metals. The second column shows the measured contact difference of potential between copper and each of the other metals, and the third column shows the amount, with respect to the copper curve, which each curve is displaced along the axis of V.

These numbers prove convincingly that the contact difference of potential must be taken into account and that the true potential against which the electrons are moving is the reading of the voltmeter plus or minus the contact difference of potential between the plates.

TABLE II.

Metals.	Contact difference of potential (volts).	Displacement of curves (volts).
Cu-Al	1.02	1.16
Cu-Zn	.75	.70
Cu-Pb	.55	.50
Cu-Fe	.15	.25
Cu-Pt	-.11	-.14

Tables are given * showing the contact difference of potential between different metals, but it is unsafe to rely on these values for accurate work, since the state of polish, the time since polishing, and other factors change these values considerably and frequently even reverse the order of the metals in the series. The only safe procedure when making measurements in which this phenomenon must be corrected for, is to adopt some method for measuring the contact difference of potential direct at the time of the experiment. Probably many of the inconsistent results which have been published with regard to the photo-electric effect can be explained as being due to the neglect of two factors: (1) the

* Winkelmann, *Handbuch der Physik*, 1st edition, vol. iii. pp. 117-121

influence of the contact difference of potential, and (2) the change of contact difference of potential which all metals, and especially the electropositive metals, undergo with time.

6. *The Velocities of the Electrons emitted by Different Metals.*—Several physicists * have investigated the velocities of the electrons emitted by different metals and have arrived at conflicting conclusions. O. v. Baeyer and A. Gehrts found values for the maximum initial velocity of the electrons from aluminium, copper, and gold to be that velocity which would give the electrons sufficient initial kinetic energy to carry them against a difference of potential of 6.3 volts. They concluded that the maximum initial velocity for these three metals is the same. E. Ladenburg found 1.76 volts for platinum, 1.55 volts for copper, and 1.07 volts for zinc, for $\lambda = 210 \mu\mu$. Millikan and Winchester, on the other hand, found the values given in Table III., at 26° C.

TABLE III.

Metal.	Velocity.	Metal.	Velocity.
Mg	.840	Ni	1.126
Al	.738	Fe	1.215
Zn	.197	Brass	1.174
Pb	.000	Cu	1.135
Sb	.394	Au	1.215
		Ag	1.340

In view of the results of the preceding section it is evident that unless a correction is made for the contact difference of potential, an electropositive metal will give off electrons with apparently smaller velocities than those leaving an electronegative plate, even though they may actually possess equal velocities. The experiments described in this section were performed to see whether, when the contact difference of potential was corrected for, it might not be found that all metals give off electrons with equal velocities, under normal conditions.

In Table III. the elements have been arranged in the order of the usual electro-positive series; and it is evident from

* P. Lenard, *Ann. d. Phys.* p. 149 (1902); E. Ladenburg, *Verh. d. D. Phys. Ges.* ix, p. 503 (1907); Millikan & Winchester, *Phil. Mag.* xiv, p. 194 (1907); O. v. Baeyer & A. Gehrts, *Ber. d. D. Phys. Ges.* xxi, p. 870 (1910).

the numbers given that, in general, the electropositive elements show electrons with smaller velocities than the electronegative elements. But Millikan and Winchester used little disks of these different metals fastened near the circumference of a large aluminium disk. This disk was so rotated as to bring one metal after another into the path of the ultra-violet light. Thus the contact difference of potential acting on an electron escaping toward the receiving-plate would be due to the somewhat uncertain combination of the metal disk and the aluminium wheel on the one side and the receiving-plate on the other. Furthermore, these metals were polished with emery and then heated to 400° C. in contact with the air. The writer has found that the softer metals, such as aluminium, lead, and copper, give abnormal values of the contact difference of potential when polished with emery because the particles of emery stick in the metal and modify its surface. Also, while the treatment to which these metals were subjected was useful for the particular object these experimenters had in view, yet it was such as to make the metals especially subject to the time-change in the contact difference of potential; and so it seems possible that metals may have been changed out of the usual order of the electropositive series. Thus it seems possible that if the correct values of the contact difference of potential were known and corrected for in these experiments, the electrons from the different metals might be found to possess equal initial velocities. The results of E. Ladenburg show differences which may easily be accounted for by differences in the contact difference of potential. The results obtained by O. v. Baeyer and A. Gehrts seem to contradict the results of other physicists, although there may be another explanation of their values.

With a view to testing the suggestion made in the preceding paragraph, mirror plates exactly similar to D, fig. 1, were prepared from brass, zinc, copper, and platinum. These, together with the aluminium plate, were then tested, using exactly the same procedure as had been used previously in section 5, except that now the plates D were interchanged, while the perforated box, C, was kept the same throughout. For C the nickel wire gauze box, which had become so tarnished as to have a constant electropositive character, was employed. The potential between C and B was 200 volts. The first and last curves were taken with the aluminium plate to make sure that no change had occurred in the setting of the apparatus during the series of experiments. The values, in volts, for the contact differences of potential

between the nickel box and the various plates are shown in Table IV.

TABLE IV.

Metal	Al (1).	Zn.	Brass.	Cu.	Pt.	Al (2).
Contact difference of potential. } ...	·89	·58	—·02	—·14	—·20	1·02

In fig. 7 (Pl. IX.) the first curve for aluminium is shown in the position actually found by experiment. The curve for platinum is also shown in its actual position to the left. From the table we see that the contact difference of potential between aluminium (1) and platinum is 1·09 volts. Thus to reduce the curve for platinum to what it would be if the real values of V , taking into account the contact difference of potential, were the same as in the case of aluminium (1)—we simply shift every point of the platinum curve to the right by an amount equivalent to 1·09 volts. In the same manner the readings for the other curves were all reduced to that for aluminium (1) as a standard. For the sake of clearness, only the curve for aluminium (1) is drawn; the points determined by the readings taken for the other metals, after being corrected in each case as described, are indicated but not connected together.

We now have a series of curves which, relatively to each other, are corrected for the contact difference of potential between the metals. It still remains to determine the absolute position of these curves along the axis of V . To do this, we refer back to section 4 and fig. 4 (Pl. IX.). Here if we calculate, from the amount which each curve is displaced for a given number of volts between C and B, what the position of the curve would be with zero volts, we obtain the curve (*i*), the position the curve should occupy if there were no stray field making itself felt through C. This curve is for a copper-plated box C and an aluminium plate D between which the contact difference of potential is 1·02 volts. Thus if the curve (*i*) is shifted to the left an amount equivalent to 1·02 volts, we obtain (*h*), which cuts the current axis at ·46. This calculation was repeated for the other set of curves mentioned but not shown in section 4, and the average of the two results shows that the curve for an aluminium plate should cut the current axis at ·39. This, then, is the point at which the current axis is cut by the "distribution of velocity" curve for electrons from an

aluminium plate, when there is zero contact difference of potential between the plate and the perforated box and no shift due to stray field through C.

In fig. 7 (Pl. IX.) the dotted line, $\overline{ab}$, cuts the curve for aluminium (1) at .39. Therefore if $\overline{ab}$ is taken as the current axis and the point $V=0$ is shifted to the foot of $\overline{ab}$, the curves will be entirely corrected for all differences of potential, and will therefore represent absolute values of the electron velocities.

It is evident from these curves that the velocities of the electrons given off by different metals under the action of ultra-violet light are at least so nearly equal that the differences are very small compared to the total velocities. Yet a small real difference seems to exist, for the differences between the curves are too large to be attributed entirely to experimental error. The fact that some of the curves are steeper than others suggests the possibility that the differences in the curves may not be due to any inherent difference in the velocities of the electrons, but to selective absorption of different wave-lengths by the metals. Unfortunately the iron arc gives a great range of wave-lengths, but it is hoped to investigate this point later by a different method. It may also be noticed that these results indicate a maximum initial velocity corresponding to about 4 volts.

7. *Electron Reflexion*.—That the electrons liberated by ultra-violet light are reflected to a greater or less degree from the surface of the receiving-plate, and that this reflexion can be prevented by the use of a perforated screen and an auxiliary field, was first demonstrated by O. v. Baeyer* in 1908. He showed that, by thus preventing the reflexion of electrons, the "distribution of velocity" curves are shifted to the left. Since that time many investigators have adopted this device for preventing reflexion. Ladenburg and Markau† used an auxiliary field of 50 volts. But in section 4 it was shown that such an auxiliary field produces a shift of the curves to the left which cannot be attributed to the prevention of electron reflexion. There must be some other factor contributing to the shift to the left.

In section 4, evidence was given to show that this second factor is the stray field through the perforated screen. It was suggested that curve (a), Pl. IX. fig. 4, represents the true shape of the "distribution of velocity" curve, and in section 6 it was shown that when the shift due to the stray

* *Verh. d. D. Phys. Ges.* x. p. 96 (1908).

† *Phys. Zeit.* ix. p. 821 (1908).

field and that due to the contact difference of potential are corrected for, the curve should cut the current axis at .39. It was thought that possibly the shift, heretofore attributed to the prevention of electron reflexion, might be entirely explained by the stray field. In view of the importance of the existence or non-existence of electron reflexion, this possibility was investigated, with the results shown in fig. 8 (Pl. IX.).

The perforated box C and the auxiliary field were removed and the electrons received directly on B. Curve 1 (Pl. IX. fig. 8) shows the result obtained in this manner. It has been corrected for the contact difference of potential between D and B. For comparison, curve (a), Pl. IX. fig. 4, after being corrected for the stray field and contact difference of potential shifts, is shown as curve 2. If the shift heretofore attributed to the prevention of electron reflexion were really due to the stray field, curve 1 would coincide with curve 2.

The following conclusions may now be drawn:—(1) The evidence in favour of electron reflexion remains unimpaired. In the present case it caused a shift of nearly two volts in the “distribution of velocity” curve. (2) By comparing fig. 4 and fig. 8 (Pl. IX.) it is seen that an auxiliary field of less than 8 volts is sufficient to prevent reflexion. (3) When the auxiliary field method is used, besides preventing reflexion, it causes a certain shift due to stray field which may be calculated and corrected for. (4) Of the curves in fig. 4 (Pl. IX.) curve (a) is most nearly the shape that is obtained without the disturbing influence of the perforated screen. This adds confirmation to the views taken in the discussion of fig. 4.

8. *The Shift of the Curves accompanying Photo-electric Fatigue.*—Photo-electric fatigue is the name given to the decrease in the photo-electric activity of a plate as the time since polishing increases. It was frequently noticed during the preceding experiments that there is usually a shift in the “distribution of velocity” curve, sometimes to the left and sometimes to the right, increasing with time. It has been frequently mentioned in this paper that metals, and especially the more electropositive metals, tend to become more electronegative the longer the time which has elapsed since polishing. Certainly this change in the contact difference of potential between the plates will cause a shift in the curves, either toward the right or the left accordingly as the electropositive character of the receiving or the emitting plate is changing the more rapidly. Is this change in the contact difference of potential sufficient to account

for the entire shift accompanying photo-electric fatigue? Or does the shift indicate a real change in the velocities of the electrons?

In investigating this question, the aluminium plate was used for D and the nickel box for C. As has been previously noted, this box had stood unpolished so long as to have a practically constant electropositive character. 200 volts was used between C and B. The aluminium plate was polished only at the beginning of the series of observations. Measurements were made of the contact difference of potential between C and D, and readings for "distribution of velocity" curves were taken at different intervals. The results are shown in fig. 9 (Pl. IX.) and Table V. Curves (a), (b), (c), and (d) were taken at intervals of 1, 7, 21, and 31 hours from the time of polishing. Curve (e) shows the variation of the contact difference of potential with time. Of course curves (a), (b), (c), and (d) do not mean that the size of the current was the same in each case. It will be remembered that the method of taking the readings causes each curve to reach its maximum ordinate at 1. This enables the shapes of the curves, and therefore the distributions of velocities, to be compared. But actually each curve represents a smaller current than does the curve preceding it. Curve (f) is plotted with time as the abscissa and the largest deflexion obtained in each case as the ordinate. It should give a rough indication of the rate of photo-electric fatigue in the present case.

TABLE V.

Time since polishing.	Contact difference of potential.	Shift of curves.	Maximum deflexion.
1 hr.	·90 volt.	·00	300
7	·81	·10	152
21	·73	·10	148
31	·68	·05	97

The shift of the curve as the time increases is in the direction corresponding to the decrease in the electropositive character of the aluminium plate, and the two are equal in amount within the limits of experimental error. Thus it seems that (at least when the plates have received no abnormal treatment such as making them the electrodes for an

induction-coil discharge during evacuation) the shift of the curves with time indicates neither a change in the velocities of the electrons nor in the distribution of velocities, but is accounted for entirely by the change in the contact difference of potential between the plates. It is significant that the metals, like platinum and silver, which show the least fatigue also show the least variation in contact difference of potential and the least shift of the curves with time. It is possible that there is an intimate relation between the cause of photo-electric fatigue and the cause of the time-changes in the contact difference of potential between metals.

9. *Summary.*—The results of this investigation may be summarized as follows :—

(1) The electrons moving between the emitting and receiving plates are acted on by the force due to the contact difference of potential as well as by the externally applied field. This effect must be allowed for when making measurements on the velocities of the electrons. (Section 5.)

(2) When this contact difference of potential is corrected for, it is found that different metals, under the action of ultra-violet light, give off electrons with practically equal velocities. The "distribution of velocity" curves are also nearly identical. (Section 6.)

(3) The evidence of reflected electrons remains unimpaired. (Section 7.) When a perforated screen and an auxiliary field are used to prevent this reflexion, there is a stray field through the screen which may be calculated and corrected for. (Section 4.)

(4) The shift of the "distribution of velocity" curves with time (when the metal has received no abnormal treatment) is accounted for by the time-changes in the contact difference of potential between the emitting and receiving plates. (Section 8.)

In conclusion I wish to express my thanks to Professor O. W. Richardson for suggesting this problem and my appreciation of his continual interest and help during the investigation.

Palmer Physical Laboratory,
Princeton, N. J.
Aug. 3, 1911.

LI. *Some Applications of the Electron Theory of Matter.* By
O. W. RICHARDSON, *Professor of Physics, Princeton University* *.

§ 1. **A**LTHOUGH parts of this paper may appear to be disconnected it is, on the whole, a development along the direction suggested by a recent communication to this Journal †. § 2 gives the results of an investigation undertaken to obtain information about the law of force which governs the collisions of electrons in metals. After I had finished this part of the investigation I found that formulæ identical with those obtained had already been published in a Danish dissertation by Niels Bohr ‡. As, however, Bohr's mathematical methods appear to be different from those which I have used, I have thought that a brief account of my calculations might prove to be of interest. § 3 contains a thermodynamic calculation of the electronic pressure outside a metal which brings the electronic emission into relation with thermoelectric phenomena. § 4 deals with the reflexion of the electrons which strike the surface of a body under conditions of thermal equilibrium and, by making use of statistical principles, deduces certain laws which have to be satisfied by such reflexion. § 5 is a further development of the theory of thermoelectric phenomena. The main point is that there is not necessarily any simple relation between thermoelectric effects and the free electrons which determine the electrical conductivity. § 6 discusses the role of "polarization" electrons in electrical conduction, largely from the point of view of the way in which galvanomagnetic phenomena may possibly be affected thereby. § 7 deals with the application of thermodynamics and statistical principles to the æthereal radiation and photoelectric effects. The close similarity between thermionic emission and the photoelectric emission arising from the complete æthereal radiation is brought out. Some of the consequences of theories of the photoelectric effect of the type of Einstein's are analysed. Finally certain equations are deduced which have to be satisfied by the functions which represent the distribution of velocity among the electrons given out under the action of light of a given frequency and otherwise of definite specification. Some of the results of this section are strictly true only for types of matter having rather restricted properties. The limitations thus introduced are considered.

* Communicated by the Author.

† Richardson, *Phil. Mag.* [6] vol. xxiii. p. 263 (1912).

‡ "Studier over metallernes Elektronentheori." Afhandling for den filosofiske Doktorgrad af Niels Bohr. Copenhagen, 1911.

§ 2. *Electrical and Thermal Conductivity and the Law of Force which governs the collisions of Electrons in metals.*

Lorentz* has shown how to calculate the electric and thermal conductivities of metals, without ignoring the existence of Maxwell's law of distribution of velocity among the electrons, on the assumption that the collisions take place with hard immovable elastic spheres. This assumption has been made, not because it is especially likely to correspond with nature, but because it simplifies the calculations. It appears, however, that this restriction is not necessary, and that the same type of calculation may be applied to the hypothesis that the collisions take place with immovable point centres of force which act on the electrons with a force equal to K/d^s , where d is distance and K is positive when the forces are repulsive. In what follows I shall adopt Lorentz's notation as far as possible, and merely indicate the way in which his calculation has to be modified.

Let n be the number of the centres of force in unit volume, $r = \xi, \eta, \zeta$ the velocity of an electron, $f(\xi, \eta, \zeta) d\xi d\eta d\zeta$ the number of electrons whose velocity components lie between ξ and $\xi + d\xi$, η and $\eta + d\eta$, and ζ and $\zeta + d\zeta$, then the number of electrons which leave the group $\xi \eta \zeta$ in unit time owing to deflexions through an angle between 2θ and $2(\theta + d\theta)$ in an azimuth between ψ and $\psi + d\psi$ is †

$$n r f(\xi, \eta, \zeta) d\xi d\eta d\zeta b db d\psi. \quad . \quad . \quad . \quad (1)$$

Here the polar axis coincides with r and b is the perpendicular distance from the centre of force to the originally straight path of the electron, and

$$b db = \left(\frac{K(M_1 + M_2)}{M_1 M_2 r^2} \right)^{\frac{2}{s-1}} \alpha d\alpha = \left(\frac{K}{m r^2} \right)^{\frac{2}{s-1}} \alpha d\alpha,$$

where M_1 and M_2 are the masses of the particles. Since we are supposing M_1/M_2 to be very small, we can put

$$(M_1 + M_2)/M_1 M_2 = m^{-1},$$

where m is the mass of an electron. The relation between θ and α is-

$$\theta = \int_0^x \left(1 - x^2 - \frac{2}{s-1} \left(\frac{x}{\alpha} \right)^{s-1} \right)^{-\frac{1}{2}} dx,$$

* 'Theory of Electrons,' p. 267.

† Maxwell's Scientific Papers, vol. ii. p. 36.

and x' is the least positive root of

$$1 - x^2 - \frac{2}{s-1} \left(\frac{x}{\alpha}\right)^{s-1} = 0.$$

Thus α is a function of θ and s only.

Evidently we may replace (1) by

$$n \left(\frac{K}{m}\right)^{\frac{2}{s-1}} r^{1-\frac{4}{s-1}} f(\xi, \eta, \zeta) d\xi d\eta d\zeta \alpha d\alpha d\psi. \quad \dots (2)$$

Now consider the reverse collisions which bring new electrons into the group. Each orbit lies in a plane, the plane containing b and r , and is symmetrical about a plane perpendicular to that of the orbit containing the apsidal distance. The magnitude of r is constant throughout a collision, the effect being simply to rotate r through the angle 2θ . The various components ξ, η, ζ will, however, be changed, let us say to ξ', η', ζ' . The new values may be written down by making use of the fact that the component of velocity along the apsidal distance has been reversed whilst the perpendicular component is unaltered. Thus, if $\psi=0$ is the plane containing r and ξ ,

$$\xi' = \xi - 2\xi \sin^2 \theta + \sqrt{\eta^2 + \zeta^2} \sin 2\theta \cos \psi, \quad \dots (2a)$$

with similar expressions for η' and ζ' .

The particles $f(\xi, \eta, \zeta) d\xi d\eta d\zeta$ may be represented by a distribution of points occupying an element of volume $d\xi d\eta d\zeta$ in a three-dimensional velocity diagram. The volume $d\xi' d\eta' d\zeta'$ occupied by the deflected points will be equal to $d\xi d\eta d\zeta$, since the new points may be obtained by reflecting the undeflected points in a plane perpendicular to the orbit and tangential to it at the apse. Thus, in considering the reverse collisions which bring extraneous electrons into the group $f(\xi, \eta, \zeta) d\xi d\eta d\zeta$, the only change we require to make in (2) is the replacement of $f(\xi, \eta, \zeta)$ by $f(\xi', \eta', \zeta')$.

In this way we arrive at the equation

$$n \left(\frac{K}{m}\right)^{\frac{2}{s-1}} r^{1-\frac{4}{s-1}} \iint \{f(\xi', \eta', \zeta') - f(\xi, \eta, \zeta)\} \alpha d\alpha df = X \frac{\partial f}{\partial x} + \xi \frac{\partial f}{\partial x} \dots (3)$$

for the stationary state in which f is independent of y and z . The left-hand side is the rate of change of f owing to collisions, and the right-hand side that which arises from the displacement of the group of electrons as a whole. Following

Lorentz, we assume that the presence of an electric current or a temperature gradient in the metal only causes a small variation from the normal Maxwell distribution, and try the solution

$$f(\xi, \eta, \zeta) = Ae^{-hr^2} + \xi \chi(r)$$

when $\chi(r)$ is a function of r alone. The reason for trying this particular form of solution is that $\xi \chi(r)$ contributes nothing to the integrals which express the number per unit volume and mean kinetic energy of the electrons, which are therefore correctly given by

$$N = A \sqrt{\frac{\pi^3}{h^3}} \quad \text{and} \quad \frac{1}{2} m \bar{v}^2 = \frac{3m}{4h}.$$

Neglecting the χ term on the right-hand side of (3) as a small correction, we have

$$\begin{aligned} n \left(\frac{K}{m} \right)^{\frac{2}{s-1}} r^{1-\frac{4}{s-1}} \chi(r) \int_0^\infty \int_0^\pi (\xi' - \xi) \alpha d\alpha d\psi \\ = n \left(\frac{K}{m} \right)^{\frac{2}{s-1}} r^{1-\frac{4}{s-1}} \chi(r) \int_0^\infty -4\pi \xi \sin^2 \theta \alpha d\alpha \\ = \left(-2hAX + \frac{dA}{dx} - r^2 A \frac{dh}{dx} \right) \xi e^{-hr^2}. \end{aligned}$$

Thus

$$\begin{aligned} \chi(r) &= \frac{\left(2hAX - \frac{dA}{dx} + r^2 A \frac{dh}{dx} \right) e^{-hr^2}}{4\pi n \left(\frac{k}{m} \right)^{\frac{2}{s-1}} r^{1-\frac{4}{s-1}} \int_0^\infty \sin^2 \theta \alpha d\alpha} \\ &= k r^{\frac{4}{s-1}-1} \left(2hAX - \frac{dA}{dx} + r^2 A \frac{dh}{dx} \right) e^{-hr^2}, \quad (4) \end{aligned}$$

where

$$k^{-1} = 4\pi n \left(\frac{K}{m} \right)^{\frac{2}{s-1}} \int_0^\infty \sin^2 \theta \alpha d\alpha. \quad (5)$$

The definite integral in (5) is a function of s only and may be evaluated graphically when s is known. Thus $\chi(r)$ does not involve α nor ψ , and only involves ξ, η, ζ in the combination r . It is therefore the solution which we have been seeking.

The electric current density is

$$\begin{aligned} J &= 4\pi e \int_0^\infty \xi^2 \chi(r) r^2 dr = \frac{4\pi}{3} e \int_0^\infty r^4 \chi(r) dr \\ &= \frac{2\pi}{3} k e \frac{\Gamma\left(\frac{2}{s-1} + 2\right)}{h^{\frac{2}{s-1} + 2}} \left[2hAX - \frac{dA}{dx} + \left(\frac{2}{s-1} + 2\right) A \frac{1}{h} \frac{dh}{dx} \right], \\ &\quad \dots (6) \end{aligned}$$

remembering that

$$\int_0^\infty e^{-x} x^p dx = \Gamma(p+1) = p\Gamma(p).$$

The specific electrical conductivity σ is e/m times the coefficient of X in (6) when $\frac{dA}{dx}$ and $\frac{dh}{dx}$ are zero. Thus

$$\sigma = \frac{4\pi}{3} k \frac{e^2}{m} \frac{\Gamma\left(\frac{2}{s-1} + 2\right)}{h^{\frac{2}{s-1} + 1}} A. \quad \dots (7)$$

The thermal current density is

$$\begin{aligned} W &= 2\pi m \int_0^\infty \xi^2 \chi(r) r^4 dr = \frac{2\pi}{3} m \int_0^\infty r^6 \chi(r) dr \\ &= \frac{\pi}{3} km \frac{\Gamma\left(\frac{2}{s-1} + 3\right)}{h^{\frac{2}{s-1} + 3}} \left[2hAX - \frac{dA}{dx} + \left(\frac{2}{s-1} + 3\right) A \frac{1}{h} \frac{dh}{dx} \right]. \\ &\quad \dots (8) \end{aligned}$$

To find the coefficient k of thermal conductivity, we have to substitute in (8) the condition that the electric current J is zero, or

$$2hAX - \frac{dA}{dx} = -\left(\frac{2}{s-1} + 2\right) A \frac{1}{h} \frac{dh}{dx}.$$

We also have

$$\frac{1}{h} \frac{dh}{dx} = -\frac{1}{\theta} \frac{d\theta}{dx}.$$

The coefficient T of thermal conductivity is therefore

$$T = \frac{\pi}{3} \frac{km}{\theta} \frac{\Gamma\left(\frac{2}{s-1} + 3\right)}{h^{\frac{2}{s-1} + 3}} A. \quad \dots (9)$$

The ratio of the thermal to the electrical conductivity is

$$T/\sigma = \frac{1}{4} \frac{m^2}{e^2 \theta} \frac{\frac{2}{s-1} + 2}{h^2} = \frac{2s}{s-1} \frac{R^2}{e^2} \theta, \quad . \quad . \quad . \quad (10)$$

if R is the constant in the equation $pv = R\theta$ reckoned for one molecule of any gas.

The calculations may be checked by putting $s = \infty$. In that case the collisions will be like those between hard elastic spheres. On making the substitution, the formulæ for σ , T , and T/σ are found to be the same as those obtained by Lorentz, when the difference in the measuring of the constant k is allowed for.

The fact which makes these calculations of interest is the known experimental result that the value of T/σ is proportional to the absolute temperature θ and is almost constant at constant temperature for all the pure metals that are good conductors of electricity. This value is very nearly equal to $3 \frac{R^2}{e^2} \theta$. It follows, in the case of such metals at any rate, that $\frac{2s}{s-1} = 3$ very nearly : whence $s = 3$.

We therefore conclude that the collisions of the free electrons inside metals do not occur with hard elastic spheres but with centres of force ; and that the force exerted on the electrons varies as the inverse third power of the mutual distance.

Some of the metals, notably iron and bismuth, have values of T/σ which are considerably above the normal. The question arises as to whether the law of force is different in these cases. I think the most reasonable hypothesis to make is that the law of force is the same in all cases, unless quite definite reasons can be adduced for abandoning such a position. Now the exceptional elements are either such as have very small electrical and thermal conductivities, or are elements which are difficult to obtain in the pure state in a suitable form for experimenting with. In the case of bad conductors the theory will be in error, because we have neglected the transference of heat of the type which occurs in electrical insulators. This would make the calculated values of T/σ less than the observed values. On the other hand, it does not seem advisable to pay much attention to the value of T/σ for metals whose purity is under suspicion, as there is something about alloys—possibly the

thermo-electric resistance suggested by Lord Rayleigh—which causes them to have a high value of the ratio.

It is of interest to note that this is not the only line of reasoning which leads to the inverse third-power law of force for the collisions of electrons in metals. Sir J. J. Thomson* showed, from his calculation of the emission of radiant electromagnetic energy from hot metals, on the assumption that it was due to the acceleration of the free electrons, that for Stefan's law and Wien's displacement law to be satisfied, it was necessary that the law of force during collisions should be the inverse third. Thomson also obtained a formula for the radiation of given frequency, which resembled Planck's formula in the case of both high and low frequencies. From a comparison of the constants it was possible to deduce the strength of the centres of force. Jeans† has confirmed Thomson's result so far as the inverse third-power law of force is concerned, but has raised the objection that the centres of force are so strong that the electrons would never get as near to them as it is known, on other grounds, that they must be all the time. This objection would not seem to hold if the centres were attractive or, like doublets, attractive in one direction and repulsive in another. The calculations in these cases, however, are much more complicated, as it is necessary to take into account the electrons which are executing closed orbits.

From the magnitude of the electrical conductivity we may obtain an estimate of the strength K of the centres of force. Putting $s=3$ in formula (7) we find

$$\sigma = \frac{2\sqrt{2}}{3\pi^{3/2}} \frac{N}{n} \frac{e^2}{K} \left(\frac{R}{m}\right)^{1/2} \frac{\theta^{1/2}}{\int_0^\infty \sin^2 \phi \alpha d\alpha}, \quad \dots \quad (11)$$

where N is the number of free electrons in 1 c.c.

Thus

$$K = \frac{2\sqrt{2}}{3\pi^{3/2}} \frac{N}{n} \left(\frac{\nu R}{\nu m}\right)^{1/2} \frac{e^2}{\sigma} \frac{\theta^{1/2}}{\int_0^\infty \sin^2 \phi \alpha d\alpha}, \quad \dots \quad (12)$$

where ν is the number of molecules in 1 c.c. of a gas at 0°C . and 760 mm. pressure.

When $s=3$, I find

$$\int_0^\infty \sin^2 \phi \alpha d\alpha = 4\pi^2 \int_0^{\pi/2} \frac{\psi \cos^2 \psi d\psi}{(\pi^2 - 4\psi^2)^2} = .396. \quad (13)$$

* Phil. Mag. vol. xiv. p. 217 (1907); vol. xx. p. 238 (1910).

† Phil. Mag. vol. xx. p. 642 (1910).

Thus all the quantities on the right of (12) are known except N and n . The best estimates indicate that for the good conductors N is a moderate fraction of the number of atoms p in unit volume of the material. Let us put $N = \gamma p$, then γ probably varies between 0.1 and 0.5 for the different good conductors. Nothing is known of the structure of the centres of force: they may either be atoms or subatomic structures, but it is unlikely that they are polyatomic. If we put $n = \delta p$ it is probable that δ will have unity as a lower limit.

Let us apply formula (12) to the case of silver. Substituting the values $\sigma = 6 \times 10^{-4}$ e.m. unit, $\nu R = 3.72 \times 10^3$ ergs/° C., $\nu m = 5 \times 10^{-8}$ gm., $e = 1.6 \times 10^{-20}$ e.m. unit, $\theta = 273^\circ$ C., and $\int_0^\infty \sin^2 \phi \alpha d\alpha = .396$, we find

$$\frac{\delta}{\gamma} K = 8.5 \times 10^{-26}. \quad . \quad . \quad . \quad . \quad (14)$$

From the constants in the radiation formula, Thomson estimates K as 2×10^{-27} , while Jeans gives 3×10^{-27} . Thus these very different methods of estimating K lead to quantities of the same order of magnitude.

Substituting the mean 2.5×10^{-27} of the two radiation estimates of K in (14), one finds $\delta/\gamma = 34$. If $\gamma = \frac{1}{3}$ for silver this would give $\delta = 11$, indicating that the centres of force are subatomic structures. A similar conclusion results in the case of the other good conductors.

There is a superficial inconsistency in formula (12), inasmuch as σ is known to be proportional to θ^{-1} for the pure metals. However, N probably varies with θ , and very likely n also. The elementary theory of the Thomson effect leads to the view that $N \propto \theta^{+3/2}$, which would make $\sigma \propto \theta^2$ if n were constant. It is probable that the N which occurs in thermo-electric phenomena is not the same thing as the N in equation (12). (See § 5.)

At the very lowest temperatures, according to Kammerlingh Onnes, the electrical conductivity of metals becomes enormously high. According to the present theory this would mean either that the number of the centres diminishes greatly or that their strength K becomes very small at these temperatures.

§ 3. The emission of Electrons from Hot Bodies as a function of Temperature.

In 1901 * the writer showed, from considerations similar to those made use of in the kinetic theory of gases, that the

* Camb. Phil. Proc. vol. i. p. 286.

number N of electrons emitted in unit time from unit area of a hot body at temperature θ was given by the expression

$$N = n \sqrt{\frac{R\theta}{2m\pi}} e^{-\omega/R\theta}, \quad \dots \quad (15)$$

where n is the number per unit volume of the free electrons inside the material, m is the mass of an electron, ω is the work it has to do in order to escape, and R is the constant in the equation $pv=R\theta$ reckoned for a single molecule. If it is assumed that n is independent of the temperature, it follows that the negative thermionic saturation current i from a hot body is of the form

$$i = A\theta^{\frac{1}{2}} e^{-\omega/R\theta}, \quad \dots \quad (16)$$

where A is independent of temperature.

Formula (15) has been deduced theoretically in an independent manner by Sir J. J. Thomson* and other writers, and there seems to be no doubt that it is accurate to the extent to which n has a precise meaning, a point which will be considered in § 5. The point of chief interest in the discussion in this section is that it relates the emission of electrons to thermoelectric effects.

The following calculation is very similar to a method of computing the value of the Thomson effect which I described in the 'Philosophical Magazine,' vol. xxiii. p. 263. It assumes that the emission and absorption of electrons and the Thomson heating effect are reversible phenomena subject to the laws of thermodynamics. It also assumes that the electrons outside the conductor obey the law of a perfect gas, $pv=R\theta$. Admitting these hypotheses, the conclusions as to the *equilibrium pressure* of the external electrons appear to be exact.

Consider two conductors, A and A' , made of the same material and maintained at the absolute temperatures θ and θ' . These are of sufficiently great size and are connected by a thin conductor. The atmospheres of electrons around them are separated by a suitable insulating partition. If contact difference of potential depends upon temperature, the potential V' at the surface of A' will not be the same as the potential V at the surface of A . Around A place a potential filter at the potential $V' \dagger$. N_0 electrons are then taken out of A by means of the usual piston and cylinder arrangement at temperature θ , potential V' , and pressure p_0 .

* Phil. Trans. A. vol. cci. p. 502 (1903). See also H. A. Wilson, Phil. Trans. A. vol. ccii. p. 243 (1904), and P. Debye, *Ann. der Physik*, vol. xxxiii. p. 469 (1910).

† Cf. Phil. Mag. vol. xxiii. p. 263 (1912).

p_0 is the pressure outside the potential filter. It is not the vapour-pressure p of the electrons just outside the surface of A. By the gas laws the relation between p and p_0 is

$$\log p_0 = \log p - \frac{e(V' - V)}{R\theta}, \quad . \quad . \quad . \quad . \quad (17)$$

where e is the charge on an electron. The N_0 electrons are then caused to expand adiabatically to the temperature θ' . The expansion is continued isothermally at θ' to the pressure p' , which is the equilibrium pressure of the electrons outside of A'. They are then allowed to condense in A', and finally to run down the connecting conductor to A. Since the conductor varies in temperature from point to point, they will absorb heat in it to the amount $N_0 e \int_{\theta'}^{\theta} \sigma d\theta$, where σ is the specific heat of electricity.

The equation $\int \frac{dQ}{\theta} = 0$ gives us

$$\frac{w + e(V' - V) + R\theta}{\theta} - R \log \frac{p'}{p_0} \left(\frac{\theta}{\theta'} \right)^{\frac{\gamma}{1-\gamma}} - \frac{w' + R\theta'}{\theta'} + e \int_{\theta'}^{\theta} \frac{\sigma}{\theta} d\theta = 0,$$

where w and w' are the internal latent heats of evaporation of the electrons at θ and θ' respectively, and γ is the ratio of their specific heats at constant pressure and at constant volume.

Substituting from (17),

$$\frac{w}{\theta} - \frac{w'}{\theta'} + R \left\{ \log p - \log p' - \frac{\gamma}{\gamma-1} (\log \theta + \log \theta') \right\} + e \int_{\theta'}^{\theta} \frac{\sigma}{\theta} d\theta = 0,$$

or

$$\log p - \frac{\gamma}{\gamma-1} \log \theta + \frac{w}{R\theta} + \frac{e}{R} \int_0^{\theta} \frac{\sigma}{\theta} d\theta = A, \quad . \quad (19)$$

where A is independent of θ .

The exact relation between the equilibrium pressure of the external electrons and the temperature is therefore

$$p = A_1 \theta^{\frac{\gamma}{\gamma-1}} e^{-\frac{w}{R\theta} - \frac{e}{R} \int_0^{\theta} \frac{\sigma}{\theta} d\theta}, \quad . \quad . \quad . \quad . \quad (20)$$

where A_1 does not involve θ .

In the case of lead σ is extremely small, so that we may put

$$p = A_1 \theta^{\frac{\gamma}{\gamma-1}} e^{-\frac{w}{R\theta}}. \quad . \quad . \quad . \quad . \quad (21)$$

In fact, in the case of all the commoner elements σ is

so small that the difference between this formula and equation (20) is almost negligible. If an electron has only three degrees of freedom $\gamma=5/3$, so that

$$p = A_1 \theta^{5/2} e^{-\frac{w}{R\theta}} \dots \dots \dots (22)$$

In (21) and (22) A_1 and R are independent of θ , but the same is not true of w . It is difficult to say how w will depend on θ , but it is practically certain that it will do so. The expansion of the material alone would change the value of w . If the variation of w is small, it could probably be represented with sufficient accuracy by making w a linear function of θ . Such a property of w would make no change in the form of (21) and (22). For if we substitute $w=w_0+a\theta$, where w_0 and a are constants, in (21) we have

$$\begin{aligned} p &= A_1 \theta^{\frac{\gamma}{\gamma-1}} e^{-\frac{w_0+a\theta}{R\theta}} = A_1 e^{-\frac{a}{R}} \theta^{\frac{\gamma}{\gamma-1}} e^{-\frac{w_0}{R\theta}} \\ &= A_2 \theta^{\frac{\gamma}{\gamma-1}} e^{-\frac{w_0}{R\theta}}, \dots \dots \dots (23) \end{aligned}$$

where A_2 is independent of θ .

Thus (23) is of the same form as (21). In order to change the power of θ which multiplies the exponential factor in equations (20) to (22), it is necessary that w should contain a term proportional to $\theta \log \theta$.

In order to deduce the value of the saturation current from the equilibrium pressure, it is usual to suppose that the number of electrons emitted is equal to those returned to the metal in a given time. This state of affairs holds good, undoubtedly, under such conditions as give rise to an equilibrium pressure, but it is questionable whether the number calculated in this way is equal to the saturation current. In fact experiments have shown that a considerable proportion of these slowly-moving electrons are reflected when they strike the surface of a metal; so that the number calculated in this way will be greater than the saturation current. We do not, as yet, know enough about this phenomenon of reflexion to be able to make proper allowance for it. If we leave it out of account tentatively, we may put

$$p = \alpha N \theta^{\frac{1}{2}} = \beta i \theta^{\frac{1}{2}},$$

where α and β are independent of temperature. We then find

$$i = A_3 \theta^2 e^{-\frac{w}{R\theta}} \dots \dots \dots (23a)$$

In this formula A_3 is independent of θ , and the form of the

function will be unaltered if w is any linear function of θ . The experiments have generally been taken to indicate that i is of the form given by (16) rather than (23 a); but I am not convinced that any of them are accurate enough to distinguish between the two expressions with certainty.

By comparing the terms involving θ in equation (20) and in equation (51) below we see that

$$\sigma = \frac{1}{e} \left\{ \frac{R}{\gamma-1} - \frac{\partial w}{\partial \theta} \right\}, \quad . \quad . \quad . \quad (24)$$

and also since $e\sigma$ is small compared with $\frac{R}{\gamma-1}$ it follows that $\frac{\partial w}{\partial \theta}$ is very nearly equal to $R/(\gamma-1)$ or to $\frac{3}{2}R$, if $\gamma=5/3$.

§ 4. The Reflexion of Electrons at the surface of Conductors.

Let us consider the atmosphere of electrons which surrounds any conductor, and let us define the group of electrons which strike unit area of any surface indefinitely near the conductor in unit time as an aggregate. A little consideration will show that the reflexion of aggregates possesses properties similar to Stewart and Kirchhoff's laws for the complete electromagnetic temperature radiation.

If the electronic equilibrium pressure is p , then, as we have seen,

$$p = A\theta^{\frac{\gamma}{\gamma-1}} e^{-\frac{w}{R\theta} - \frac{e}{R}} \int_0^\theta \frac{\sigma}{\theta} d\theta = nR\theta,$$

where n is the number of electrons per unit volume of the atmosphere. The number of electrons which strike unit area of any surface in unit time is

$$\begin{aligned} N &= n \int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty n f(u.v.w) du dv dw = n \left(\frac{R}{2\pi m} \right)^{\frac{1}{2}} \theta^{\frac{1}{2}} \\ &= p(2\pi m R)^{-\frac{1}{2}} \theta^{-\frac{1}{2}} = A \cdot (2\pi m R)^{-\frac{1}{2}} \theta^{\frac{\gamma}{\gamma-1} - \frac{1}{2}} e^{-\frac{w}{R\theta} - \frac{e}{R}} \int_0^\theta \frac{\sigma}{\theta} d\theta. \end{aligned} \quad (25)$$

This is also the number of electrons emitted in the same time by the same area of a perfect absorber (*i.e.* a substance which does not reflect electrons) at the same temperature.

If the body is not a perfect absorber, then some of the above N electrons will be reflected by it. Let the proportion be r . Then the number actually absorbed by the conductor in time δt is $(1-r)N\delta t$. Let the number emitted by the same surface in time δt be $\epsilon N\delta t$. Then the equilibrium condition gives

$$\epsilon = 1-r. \quad . \quad . \quad . \quad . \quad . \quad (26)$$

Thus the emissivity (compared with a perfect absorber) and the reflecting power are complementary.

A relation of type (26) holds not only for the complete aggregate but for each individual range of velocity or momentum used in specifying it. Thus if $\epsilon(u.v.w)du dv dw$ represents the number of particles emitted in unit time with velocity components between u and $u+du$, v and $v+dv$, w and $w+dw$, $r(u.v.w)du dv dw$ the number of similar particles in the reflected group and $N(u.v.w)du dv dw$ the corresponding thing for the incident aggregate; then

$$\epsilon(u.v.w) = N(u.v.w) - r(u.v.w). \quad (26a)$$

If this equation were not true, the character of the statistically steady aggregate would change with time. Now

$$N(u.v.w) = N \times f(u.v.w),$$

where f is a probability expression calculable from Maxwell's law.

Both theory and experiment point to the conclusion that

$$\epsilon(u.v.w) = \epsilon \cdot N \cdot f(u.v.w);$$

whence it follows that

$$r(u.v.w) = r \cdot N \cdot f(u.v.w).$$

Thus the group which arises by the reflexion of a disordered aggregate is itself disordered, or the process of reflexion is of such a nature as to transform the velocity distribution of the incident aggregate into the same distribution among the reflected group.

This relation may be expressed somewhat differently as follows:—If n is the number of electrons per unit volume of the surrounding space in the state of equilibrium, then the number striking unit area of surface in unit time with velocity components between u and $u+du$, v and $v+dv$, w and $w+dw$ is

$$n \left(\frac{km}{\pi} \right)^{3/2} u e^{-km(u^2+v^2+w^2)} du dv dw$$

if u is normal to the surface. Out of this group let the proportion reflected with velocity components between u_1 and u_1+du_1 be $F(u.v.w.u_1)du_1$, the proportion with velocity components between v_1 and v_1+dv_1 be $G(u.v.w.v_1)dv_1$, and the proportion with velocity components between w_1 and w_1+dw_1 be $H(u.v.w.w_1)dw_1$. Then in the steady state at the temperature corresponding to k the total number of electrons reflected from unit area in unit time with velocity

components between u_1 and $u_1 + du_1$ is

$$n \left(\frac{km}{\pi} \right)^{3/2} du_1 \int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty F(u.v.w.u_1) u e^{-km(u^2+v^2+w^2)} du dv dw.$$

But, as we have seen, this is also equal to

$$r \cdot du_1 \cdot 2km u_1 e^{-km u_1^2} \int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty n \left(\frac{km}{\pi} \right)^{3/2} u e^{-km(u^2+v^2+w^2)} du dv dw.$$

Thus $F(u.v.w.u_1)$ has to satisfy the equation

$$\int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty u e^{-km(u^2+v^2+w^2)} \left\{ \frac{1}{r} F(u.v.w.u_1) - 2km u_1 e^{-km u_1^2} \right\} du dv dw = 0. \quad \dots (26b)$$

$G(u.v.w.v_1)$ and $H(u.v.w.w_1)$ satisfy equations which only differ from (26b) in that the expression in brackets is replaced by

$$\frac{1}{r} G(u.v.w.v_1) - \left(\frac{km}{\pi} \right)^{1/2} e^{-km v_1^2}$$

in the one case and

$$\frac{1}{r} H(u.v.w.w_1) - \left(\frac{km}{\pi} \right)^{1/2} e^{-km w_1^2}$$

in the other. Each equation is true for all values of u_1 , v_1 , and w_1 respectively and of k .

The rate at which the conductor gains heat, and the force acting on it in any direction, owing to the activity of the electrons, may be represented by integrals of the type

$$\int Q [N(u.v.w) - r(u.v.w) - \epsilon(u.v.w)] dS \cdot du dv dw, \quad (27)$$

where Q is kinetic energy in the first case and momentum in the second. All of these vanish, as they should, by virtue of (26a).

In an enclosure containing different bodies in thermal equilibrium, N will be different near different bodies on account of the contact difference of potential. The considerations just brought forward show that the occurrence of reflexion of the electrons does not affect the conclusions as to the nature of the ensuing equilibrium which were drawn in my previous paper. The effect of electromagnetic radiation and photoelectric action will be considered in a later section.

§ 5. *The Electron Theory of Contact Electromotive Force and Thermoelectricity.*

In the former paper the writer has shown how the relation between the contact electromotive forces and the various thermo-electric constants of substances, on the one hand, and the number and potential energy of the internal free electrons, on the other, may be determined. The development there given involves the implicit assumption that the internal electrons in any one substance may be treated as if they all possessed the same potential energy. It also involved the assumption that the heat liberated where electrons enter a metal is equal to the difference in their potential energy before and after condensation. The results of § 2 of the present paper show that so much simplicity is not warranted by the facts; though it may well be that the supposedly characteristic constants n and w of the previous discussion may be replaced by suitably formed average values. A more complete theory of these effects will now be given.

The state of the electrons at any point of any system is defined by the average number ν per unit volume at that point at any instant, by the average potential energy ω of the electrons at that point, and by the temperature θ , which is proportional to the average kinetic energy of the electrons. We may imagine the interior of any conductor to be mapped out by means of the level surfaces of ω . The distribution of these surfaces will be definite and characteristic for each conductor. At points just outside any conductor ω takes the constant value ω_0 . In the state of equilibrium the values of ω_0 are different and characteristic for different conductors.

This additional complexity will not affect the result which we have imported from the dynamical theory of gases, namely, that at any point in a system in equilibrium at temperature θ ,

$$dn = \nu d\tau = Ke^{-\omega/R\theta} d\tau, \dots \dots \dots (28)$$

where dn is the number of electrons which participate in thermal phenomena in the element of volume $d\tau$, and K is constant throughout the system, being a function of θ only.

We shall now consider the formulæ which determine the equilibrium between the external free electrons and the internal electrons which can become free. Confining our attention to a single conductor, consider first the special case in which there are a finite number p of finite internal regions

each characterized by constant values $\nu_1 \omega_1 \tau_1 \dots \nu_p \omega_p \tau_p$. Then if $\nu_0 \omega_0 \tau_0$ are the values of the corresponding variables just outside the conductor, we have

$$\frac{\nu_0}{e^{-\omega_0/R\theta}} = K = \frac{\nu_1}{e^{-\omega_1/R\theta}} = \dots = \frac{\nu_p}{e^{-\omega_p/R\theta}} = \frac{n}{\sum \tau e^{-\omega/R\theta}}, \quad (28a)$$

where n is the total number of electrons which can become free which are present in the system. In general it will only be possible to regard ω as having a constant value over a region of infinitesimal volume, so that

$$\frac{\nu_0}{e^{-\omega_0/R\theta}} = K = \frac{dn}{e^{-\omega/R\theta} d\tau} = \frac{n}{\int e^{-\omega/R\theta} d\tau}, \quad (28b)$$

where the integral is taken throughout the entire volume of the system. If we regard ω_0 as a fixed constant,

$$\nu_0 = n / \int_{\tau} e^{-(\omega - \omega_0)/R\theta} d\tau. \quad (28c)$$

If we consider a system containing more than one body in a state of equilibrium, the steady (contact) differences of potential will be given by equations of the type

$$e(V_m - V_p) = \omega_{0m} - \omega_{0p}, \quad (29)$$

where ω_{0m} denotes the potential energy of an electron just outside the m th body.

The next step is to calculate the absorption of heat when electrons are allowed to evaporate from a conductor. Consider the conductor to be surrounded by an insulating boundary such that the volume of the space between the conductor and the boundary is v . If the boundary is displaced so that the volume increases by dv , work $p dv$ will be done by the equilibrium pressure, p , of the atmosphere of electrons. The increment dS in the entropy of the system will be

$$dS = \frac{1}{\theta} (dU + p dv), \quad (30)$$

where

$$U = n(\frac{3}{2} R\theta + J), \quad (31)$$

$$J = \int \omega e^{-\omega/R\theta} d\tau / \int e^{-\omega/R\theta} d\tau, \quad (32)$$

$$\text{and } p = \nu R\theta. \quad (33)$$

n is the total number of electrons in the system which can become free, and the integrals in J are extended throughout the system. Since n is constant it follows that when the

volume is increased by dv the heat abstracted is

$$dQ = \theta dS = dv \left(n \frac{\partial J}{\partial v} + \nu R \theta \right). \quad . \quad . \quad . \quad (34)$$

The value of $\frac{\partial J}{\partial v}$ which we require is the limiting value which obtains when v is infinitesimal compared with τ , the volume of the conductor. We have

$$\begin{aligned} J_{\tau+\delta v} &= \frac{\int_{\tau+\delta v} \omega e^{-\omega/R\theta} d\tau}{\int_{\tau+\delta v} e^{-\omega/R\theta} d\tau} = \frac{\int_{\tau} \omega e^{-\omega/R\theta} d\tau + \int_{\delta v} \omega e^{-\omega/R\theta} d\tau}{\int_{\tau} e^{-\omega/R\theta} d\tau + \int_{\delta v} e^{-\omega/R\theta} d\tau} \\ &= \frac{\int_{\tau} \omega e^{-\omega/R\theta} d\tau + \delta v \omega_0 e^{-\omega_0/R\theta}}{\int_{\tau} e^{-\omega/R\theta} d\tau + \delta v e^{-\omega_0/R\theta}}. \end{aligned}$$

Thus

$$\frac{\partial J}{\partial v} = \text{Lt}_{\delta v=0} \frac{1}{\delta v} \{J_{\tau+\delta v} - J_{\tau}\} = \frac{e^{-\omega_0/R\theta}}{\int_{\tau} e^{-\omega/R\theta} d\tau} \{\omega_0 - J\},$$

and from (3)

$$n \frac{\partial J}{\partial v} = \nu \{\omega_0 - J\}. \quad . \quad . \quad . \quad (35)$$

By comparison with (10), the loss of heat which accompanies the escape of one electron is

$$\frac{dQ}{\nu dv} = \omega_0 - J + R\theta. \quad . \quad . \quad . \quad (36)$$

Moreover, since S is a perfect differential,

$$\frac{\partial}{\partial v} \left(\frac{\partial S}{\partial \theta} \right)_v = \frac{\partial}{\partial \theta} \left(\frac{\partial S}{\partial v} \right)_{\theta},$$

and by using (9),

$$R\theta^2 \frac{\partial \nu}{\partial \theta} = n \frac{\partial J}{\partial v} = \nu (\omega_0 - J). \quad . \quad . \quad . \quad (37)$$

Hence

$$\nu = A e^{\int \frac{\omega_0 - J}{R\theta^2} d\theta} = A e^{-\frac{\nu_0 - J}{R\theta} + \int \frac{1}{R\theta} \frac{\partial}{\partial \theta} (\omega_0 - J) d\theta}, \quad . \quad . \quad . \quad (38)$$

where A is a quantity, characteristic of the material, which does not involve θ .

To determine the Peltier effect P we only need to consider a reversible isothermal cycle involving two different conductors. Let the suffixes 1 and 2 be used to distinguish the various physical quantities which relate to the separate materials, the notation being otherwise as before. Let eV_2 be $> eV_1$. Surround the first conductor by a potential filter,

as before, maintained at V_2 . This will reduce the pressure of the electrons from p_1 to p_1^0 and will change their potential energy from eV_1 to eV_2 but will not affect their temperature θ . The cycle consists in evaporating N electrons through the potential screen. The work done is $NR\theta$ and the heat absorbed is, by virtue of (14), $N[(\omega_0 - J)_1 + e(V_2 - V_1) + R\theta]$. Next expand at θ from p_1^0 to p_2 . The work done and heat absorbed are each equal to $NR\theta \log(p_1^0/p_2)$. Next condense at V_2 and p_2 in the second body. The work done is $-NR\theta$ and the heat absorbed is $-N[(\omega_0 - J)_2 + R\theta]$. During the flow along the wire connecting the conductors there is no work done, but there is an absorption of heat NP_e at the junction, where P is the Peltier effect. The total amount of work in this isothermal reversible cycle is $NR\theta \log p_1^0/p_2$; so that $p_1^0 = p_2$. The total absorption of heat is

$$N \left[(\omega_0 - J)_1 + e(V_2 - V_1) + R\theta + R\theta \log \frac{p_1^0}{p_2} - (\omega_0 - J)_2 - R\theta + Pe \right],$$

and since

$$\omega_{01} - \omega_{02} = e(V_1 - V_2)$$

we have

$$Pe = J_1 - J_2. \quad (39)$$

The expression for the Thomson effect (specific heat of electricity) may be obtained by considering a cycle which differs from the foregoing in that there is now only one conductor but its ends are maintained at different temperatures. By applying the equation $\int \frac{dQ}{\theta} = 0$ to the same set of processes as were considered in the elementary theory, we arrive at the equation

$$e \int_{\theta'}^{\theta_0} \frac{\sigma_1}{\theta} d\theta + \frac{(\omega_0 - J)_1}{\theta_0} - \frac{(\omega_0 - J)_1'}{\theta'} + \frac{e(V' - V_1)}{\theta_0} - R \log \frac{p_1'}{p_1^0} - \frac{R\gamma}{\gamma - 1} \log \frac{\theta_0}{\theta'} = 0.$$

The dashed quantities refer to the temperature θ' and the undashed to θ_0 , the notation being in fact the same as before. From the conditions of equilibrium among the electrons in the parts of the system which are at the same temperature we have

$$\left. \begin{aligned} \log p_1^0 &= \log p_1 - e \frac{V_1' - V_1}{R\theta_0}, \\ \log p_1' &= \log \frac{n_1' R \theta'}{\tau_1'} - \log \frac{1}{\tau_1'} \int_{\tau_1'} e^{-(\omega - \omega_0)/R\theta'} d\tau, \\ \log p_1 &= \log \frac{n_1 R \theta_0}{\tau_1} - \log \frac{1}{\tau_1} \int_{\tau_1} e^{-(\omega - \omega_0)/R\theta_0} d\tau, \end{aligned} \right\}$$

whence

$$e \int_{\theta'}^{\theta_0} \frac{\sigma_1}{\theta} d\theta - \frac{J_1}{\theta} + \frac{J_1'}{\theta'} - R \log [n_1' / \int_{\tau_1'} e^{-\omega/R\theta'} d\tau] \\ + R \log [n_1 / \int_{\tau_1} e^{-\omega/R\theta} d\tau] - \frac{R}{\gamma-1} \log \left(\frac{\theta}{\theta'} \right) = 0.$$

Thus

$$e \int_0^{\theta_0} \frac{\sigma_1}{\theta} d\theta - \frac{J_1}{\theta_0} + R \log K - \frac{R}{\gamma-1} \log \theta_0 = A,$$

where A is independent of θ , and $K = n \div \int_{\tau} e^{-\omega/R\theta} d\tau$ is a function of θ but is the same for all substances. Differentiating by θ_0 , we have

$$\sigma_1 = \frac{1}{e} \left[\frac{R}{\gamma-1} + \theta \frac{\partial}{\partial \theta} \left(\frac{J_1}{\theta} - R \log K \right) \right]. \quad (40)$$

This equation is consistent with (24) since $w = \omega_0 - J$ by (36), $\log K = \log \nu + \frac{\omega_0}{R\theta}$ by (28 b) and $R\theta^2 \frac{\partial \nu}{\partial \theta} = \nu(\omega_0 - J)$ by (37). For the thermo-electromotive force T of a circuit we have

$$T = P_{\theta'} - P_{\theta} + \int_{\theta_0}^{\theta'} (\sigma - \sigma_1) d\theta.$$

Thus, in virtue of (17) and (21), since K is independent of the material,

$$Te = J_1' - J_2' - J_1 + J_2 + \int_{\theta_0}^{\theta'} \theta \frac{d}{d\theta} \left(\frac{J_2 - J_1}{\theta} \right) d\theta \\ = \int_{\theta_0}^{\theta'} \frac{J_1 - J_2}{\theta} d\theta, \quad (41)$$

and the thermoelectric power of the circuit is

$$\frac{\partial T}{\partial \theta} = \frac{1}{e} \frac{J_1 - J_2}{\theta} = \frac{P}{\theta}. \quad (42)$$

(23) is derived from (22) by differentiating by θ' and dropping the suffix.

Since $\nu = Ke^{-\omega/R\theta}$ we have

$$J_1 = \left. \begin{aligned} & \int_{\tau_1} \frac{\nu}{K} \{ R\theta \log K - R\theta \log \nu \} d\tau \\ & \int_{\tau_1} \frac{\nu}{K} d\tau \\ & = R\theta \log K - \frac{R\theta}{n_1} \int_{\tau_1} \nu \log \nu d\tau \\ & = R\theta \log K - \frac{R\theta}{n_1} \int_{n_1} \log \frac{dn}{d\tau} dn; \end{aligned} \right\} \quad (43)$$

whence

$$Pe = J_1 - J_2 = R\theta \left\{ \frac{1}{n_2} \int_{n_2} \log \frac{dn}{d\tau} dn - \frac{1}{n_1} \int_{n_1} \log \frac{dn}{d\tau} dn \right\} \quad (44)$$

and

$$\sigma = \frac{1}{e} \left[\frac{R}{\gamma - 1} - \frac{R}{n_1} \int_{n_1} \log \frac{dn}{d\tau} dn \right]. \quad . \quad . \quad . \quad (45)$$

Thus the formulæ of the more complete theory only differ from the formulæ of the simple theory, which treats the internal free electrons (ν_1 per unit volume) as if they were all alike, by the substitution of $\frac{1}{n_1} \int_{n_1} \log \frac{dn}{d\tau} dn$ for $\log \nu_1$. In the new formulæ n_1 is the total number of electrons which can become free which are contained by the conductor considered.

The present theory removes a number of contradictions with experiment which the simpler theory exhibited. In particular there is no reason to expect any very close connexion between the Peltier effect and the difference in the electrical conductivity of the substances concerned. Koenigsberger and Weiss* have recently shown that the Peltier effect at the junction between a very poor and a very good conductor is not in general of exceptional magnitude and in some cases is in the opposite direction to that required by the simple theory. The present theory requires that not only those electrons which are free, in the sense that they can take part in conveying the current, should be taken into account, but also those which are potentially capable of entering this class by means of the dynamical actions which actually occur. There may be a large number of the latter in the very worst conductors, and there is, so far as I am aware, no way of determining the integrals which occur in (44) except by thermoelectric and thermionic measurements. Similar considerations apply to the large Peltier effect which, as Sir J. J. Thomson pointed out, should, on the simpler theory, be found to occur between the liquid and solid phase at the melting-point. An argument from phase-rule considerations may be used to prove the equality of J_1 and J_2 for the two phases in equilibrium; but as I am not sure that such an application of the phase rule is legitimate, I do not wish to press this point at present. At any rate there is no reason to expect a large Peltier effect in this case, and the experiments of Wiedemann, Cermak, and others have shown that any such effect, if it exists, is exceedingly small.

* *Ann. der Physik*, vol. xxxv. p. 1 (1911).

The foregoing formulæ are, naturally, consistent with the results of Kelvin's theory of thermoelectric phenomena. The more general theory does not make any vital change in the conclusions about contact electromotive force to which the simple theory led us.

As regards the relation between thermoelectric effects and electrical conductivity, the natural assumption to make would be, that whereas both the electrons which execute closed, and those which execute open, orbits play a part in thermoelectric phenomena, conductivity is only concerned with those which execute open orbits.

§ 6. *Polarization Electrons and Galvanomagnetic Phenomena.*

A point which deserves mentioning is the part possibly played by polarization electrons in metallic conduction. It is likely enough that in the interior of the metal there are a number of electrons which behave in a similar manner to those in a dielectric. In that case there will be some regions in the interior where the part of the electric intensity *which reverses with the external electromotive force* will be greater and others where it will be less than the average. It is even likely enough that the sign of the electric intensity will be reversed in some parts. Such a state of things might make a good deal of difference in the electrical conductivity and also in the magnitude of galvanomagnetic effects. Whether they would be important or not would depend on the strength of the polarization and the ratio of the linear scale of its parts to the free path of an electron.

As an extreme illustration we may take the mean free path to be small compared with the scale of the polarization. Let us suppose that the structure of the medium is so simple that we may divide it up into two classes of regions, A and B, in one of which (A) the electric intensity is X_1 and in the other (B) it is $X_2 = \alpha X_1$. Let n_1 and n_2 be the average number of free electrons per unit volume, T_1 and T_2 their mean free times, δT_1 and δT_2 the alterations of T_1 and T_2 produced by a magnetic field, S_1 and S_2 the average areas of cross-section per unit area of an intersecting plane, and a_1 and a_2 the average lengths per unit length cut off a line by the two classes of regions. In each case the suffixes refer to the corresponding class of region. The simple type of electron theory, which assumes all the electrons to have the same velocity of agitation and all those of the same class to

move for the same time between collisions, leads to

$$\sigma = \frac{1}{2} \frac{e^2}{m} \frac{n_1 S_1 T_1 + \alpha n_2 S_2 T_2}{a_1 + \alpha a_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (46)$$

$$\frac{Y_0}{H_0 X_0} = - \frac{1}{3} \frac{e}{m} \frac{n_1 S_1 T_1^2 + \alpha n_2 S_2 T_2^2}{n_1 S_1 T_1 + \alpha n_2 S_2 T_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (47)$$

$$\frac{\delta R}{R} = \frac{\frac{1}{12} \frac{e^2}{m} H_0^2 (n_1 S_1 T_1^3 + \alpha n_2 S_2 T_2^3) - (n_1 S_1 \delta T_1 + \alpha n_2 S_2 \delta T_2)}{n_1 S_1 T_1 + \alpha n_2 S_2 T_2} \quad . \quad . \quad . \quad (48)$$

Here σ is the specific electrical conductivity, $Y_0/H_0 X_0$ is the Hall coefficient, and $\delta R/R$ is the change of resistance in a transverse magnetic field H_0 .

The point of chief interest is that, as α may very well be negative, the sign of the fraction in (37) might easily be determined by the value of the ratio T_2/T_1 . Thus we have a means of accounting for the oscillation of sign of the Hall effect in the non-magnetic metals without having recourse to magnetic perturbations. On the other hand, we should rather expect oscillations in $\delta R/R$ if this is the explanation of the apparent instability of the Hall effect, unless the T^3 terms are swamped by the δT terms in (38), which, as E. P. Adams * has pointed out, may easily happen.

I do not think that formulæ (46) to (48) should be taken as more than illustrative. The current evidence indicates that the mean free path is larger than the probable scale of the polarization structure. Moreover, formula (46) would seriously disorganize the law of Wiedemann-Franz-Lorenz. It seems probable that considerations of this kind will enter as corrective terms of the main factors. They may be of especial importance in the calculation of the conductivity for periodic electromotive forces.

§ 7. *On Photoelectric and Related Phenomena.*

We shall now consider the conclusions to which we are led when we apply statistical and thermodynamical principles to photoelectric phenomena. In the preceding paper I considered the state of equilibrium which results when we have a number of different material substances in an insulated enclosure, on the assumption that interchange of energy and electric charge between the different bodies and the surrounding space and each other could take place in

* Phys. Rev. vol. xxiv. p. 428 (1907).

virtue of electric and thermal conduction and thermionic emission. The result of that investigation may be summarized in the statement that at any point inside the enclosure where the time average of the potential energy of an electron is ω and the time average of the number of electrons per c.c. is n , then

$$R \theta \log n + \omega = C. \quad . \quad . \quad . \quad . \quad (49)$$

C is constant at every point inside the enclosure but may be a function of temperature. In general there will be a steady average field of electric force inside the enclosure dependent upon the natural contact difference of potential of the enclosed bodies. Thus n will vary from point to point of the space of the enclosure as well as in the interior of the material bodies.

Now electronic emission is not the only means of interchange of energy and electric charge between bodies not in contact which is universally operative. To it we must certainly add electromagnetic radiation and in all probability photoelectric action as universal properties of matter. It may seem strange to those unfamiliar with the phenomena, thus to postulate the universality of electronic emission. A little consideration, however, will show that in its relations to matter and to temperature, electronic emission is in precisely the same general position as electromagnetic "æthereal" radiation. All bodies radiate æthereally in a perceptible manner at high temperatures just as all bodies, being conductors of electricity, emit electrons under similar conditions. At ordinary temperatures most, but not all, bodies cease to emit electrons in measurable quantity just as many transparent bodies cease to emit æthereal radiation in measurable quantity. The difference in this respect is exaggerated by the more rapid temperature variation of the electronic as compared with the æthereal emission. The really important difference is that the electronic radiation is affected by a field of electric force, whereas the æthereal radiation is not. This causes the electronic radiation from an isolated body very rapidly to become infinitely slow, whereas there is no such effect on the æthereal radiation.

In general, then, we have to consider interchanges to be taking place by virtue of conduction, electronic emission, æthereal radiation, and photoelectric action. Any perfectly reflecting enclosure containing real bodies in thermal equilibrium will be filled with æthereal radiation which will give rise to photoelectric emission. The enclosure will, therefore, contain an atmosphere of electrons even when the materials have no thermionic emissivity; if we keep the term thermionic

emission for the direct dynamical escape of the electrons in virtue of their kinetic energy exceeding the work of the surface forces. It will not necessarily be possible to distinguish, by statistical or thermodynamical methods, between the photoelectric or thermionic origin of the electrons. We shall therefore try, first of all, to find out what we can about the nature of the æthereal radiation and of the atmosphere of electrons in the statistically steady distribution without considering their origins.

In the first place, the complete æthereal radiation will be identical in constitution at every point of the enclosure. This may be shown by bringing the enclosure into connexion with any other enclosure at the same temperature. The æthereal radiations may be allowed to intermingle by opening partitions provided with optically transparent diaphragms which prevent the flow of electrons. If there is any net transference of æthereal energy under these conditions, the system may be made to violate the second law of thermodynamics. The equality which thus follows holds not only for the energy of the complete radiation, but also for each range of wave-length, for each plane of polarization and for each direction of propagation; as may be shown by inserting known devices for limiting the waves transmitted. As the equivalence holds independently of the shape and contents of the enclosures and of the position of the point of contact, it follows that the transmissivity of the complete æthereal radiation is identical at every point and that its nature is determined solely by the temperature. Thus Stewart and Kirchhoff's conclusions about the nature of the æthereal radiation are unaffected by the occurrence of thermionic and photoelectric emission.

For the present I wish to avoid discussion of the vexed question of the nature of the interaction between the material parts of the system and the æthereal radiation and to confine my remarks to the conclusions which may be drawn from the existence of a statistically steady condition of the æthereal and electronic radiations. The immediate problem may be thus stated:—An isolated system contains a certain amount of energy. This is divided between the æthereal vibrations and the material part of the system in a way which is perfectly definite but which we leave undetermined. There is, therefore, a definite but undetermined amount of energy to divide among the electrons and the other material portions of the system. The problem which we require to solve is, how is the energy divided among the electrons under these circumstances?

The true answer will be given if the radiation is entirely ignored. For, if we compare the two states when the radiation is present and when it is not, in the former case every particle which has lost energy by radiation will be compensated for by another which has just gained an identical amount from the radiation. Thus the two cases are statistically identical except for the energy of the æthereal radiation, and the problem becomes the well-known problem of statistical mechanics. The solution is

$$dn = A e^{-(\omega + L)/R\theta} dx_1 dx_2 dx_3 dp_1 dp_2 dp_3, \quad (49 a)$$

where dn is the number of particles whose coordinates lie between x_1 and $x_1 + dx_1$ &c., and whose momenta lie between p_1 and $p_1 + dp_1$ &c.* A is constant throughout the system, and may be determined in terms of the total number of particles (electrons) by integrating throughout the system. The potential energy ω is a function of $x_1 x_2 x_3$ and the kinetic energy L is a quadratic function of the momenta $p_1 p_2 p_3$. It follows that the average kinetic energy of the electrons is independent of their potential energy and is equal to $\frac{3}{2}R\theta$, and also that the average number n per unit volume at a point where the potential energy of an electron is ω is given by

$$R\theta \log n + \omega = C.$$

Thus equation (49) still holds good when photoelectric actions are considered to be operative in liberating the electrons, as well as thermionic emission.

The æthereal radiation may be shown to obey Stefan's law and Wien's law by the usual methods of proof if the appliances are slightly modified. We may separate the æthereal radiation from the electronic atmospheres by means of an ideal transparent solid devoid of thermionic and photoelectric emission. The radiations may subsequently be allowed to intermingle in a reversible manner through a similar filter. The dynamical operations are carried out in perfectly reflecting enclosures lined with the same transparent non-emissive material. In this way the complications arising from the presence of an electronic atmosphere mixed with the æthereal radiations are avoided, and one arrives at the usual results that the total radiation density

$$= \int E_\lambda d\lambda = A_1 \theta^4 \quad \text{and} \quad E_\lambda = A_2 \theta^5 \phi(\lambda \theta),$$

where A_1 and A_2 are universal constants.

The relation between the concentration (number per unit

* Jeans, *loc. cit.* p. 70.

volume) of the electrons in the atmosphere inside an enclosure, bounded by any single material substance, and its temperature, may be determined in the following manner. Imagine a cylindrical box made of the material substance. The sides and top of the box are covered with a layer of the ideal transparent non-emitting substance, but the bottom surface is exposed to the interior. A piston made of the ideal transparent substance works up and down the cylinder and is initially at the bottom. The enclosure then contains æthereal radiation alone. Its walls are externally in thermal and electrical contact with an indefinitely large mass of conducting matter at the same temperature. As the piston moves up the amount of æthereal radiation in the enclosure remains constant, but the space below the piston becomes filled with the electrons emitted by the substance. These exert a pressure p on the piston. There is no work done by the pressure arising from the radiation as the density of this is always the same on both sides. By moving the piston up and down, the electrons may be pumped out of and into the material in a reversible manner.

Let v be the volume below the bottom face of the piston-head, n the number of electrons per unit volume in the same space, e the charge on an electron, ϕ the difference in the energy of the system due to the escape of a single electron, then the change in U , the energy of the system, produced by a motion of the piston, is

$$dU = d(nv\phi).$$

The corresponding increment of entropy is

$$dS = \frac{1}{\theta} (dU + p dv) = \frac{1}{\theta} \{ (p + n\phi) dv + v d(n\phi) \}.$$

Since S is a perfect differential when v and θ are the independent variables

$$\theta \frac{\partial p}{\partial \theta} = p + n\phi + v \frac{\partial}{\partial v} (n\phi) = p + nw, \quad . \quad . \quad (50)$$

where w is the latent heat of evaporation reckoned for a single electron, and since $p = nR\theta$,

$$n = A e^{\int \frac{w}{R\theta^2} d\theta}, \quad . \quad . \quad . \quad . \quad (51)$$

where A is a constant, characteristic of the material but independent of θ .

Equation (51) expresses the relation between the equilibrium concentration of the electrons in the atmosphere

close to the surface of any substance quite apart from the mode of emission. Thus the same type of relation would be satisfied by the electrons emitted thermionically if there were no photoelectric action, and by the electrons emitted by the *complete* æthereal radiation if there were no thermionic emission. In fact (51) is entirely consistent with the results of a calculation of the thermionic emission based on the simple hypothesis that there are free electrons inside the metal which escape in virtue of their kinetic energy exceeding the work which is necessary for them to escape from the surface.

The question at once suggests itself as to whether any true thermionic emission really exists, or in other words, whether what is usually considered to be thermionic emission is not in reality the photoelectric emission of the material arising from the æthereal radiation at the temperature of the experiments. This is a view which occurred to me as a possibility many years ago, and I think the balance of experimental evidence is against it. When one considers the large electronic emission of hot platinum and carbon and reflects upon the intensity of a beam of ultra-violet light which would be required to produce an equal effect photoelectrically, the probability of such a view being correct becomes exceedingly small. On the other hand the problem, considered from this standpoint, involves the comparative penetrability of light and slow moving electrons, a matter about which very little is known.

Leaving this question aside, let us see what we can find out about the connexion between photoelectric emission and the light which causes it. For the present we shall suppose that we are dealing with a material which is photoelectrically active but has no thermionic emission. No such material may exist, but the assumption simplifies the discussion and, as we shall see later, the results will probably be applicable to the case of real bodies. We shall suppose the material to be in a perfectly reflecting enclosure and the steady state characteristic of the temperature θ to have been established. We may assume the photoelectric emission to be dependent either upon the density of the æthereal radiation present or upon its rate of absorption. We shall take the latter as being the more general. Our results can then be adapted to the former hypothesis by making the emissivity ϵ equal to unity. Let the steady energy density of the vibrations whose frequencies lie between ν and $\nu + d\nu$ be $E(\nu)d\nu$, then the energy emitted per unit time which is

comprised between those wave-lengths is

$$\frac{c\epsilon}{4} E(\nu) d\nu, \quad . \quad . \quad . \quad . \quad . \quad . \quad (52)$$

where c is the velocity of light. Let us suppose that the emission or absorption of unit quantity of radiant energy of frequency ν at the temperature θ causes the liberation of $F(\nu\theta)$ electrons. Then the total number of electrons emitted in unit time by the complete radiation is

$$N = \frac{c}{4} \int_0^\infty \epsilon F(\nu\theta) E(\nu) d\nu. \quad . \quad . \quad . \quad . \quad (53)$$

But this number must be equal to the number of electrons returned to the body per unit time from the external atmosphere. Now the electrons behave like the molecules of a gas (since they satisfy equations (49) and (49 a)), so that the number which reach the emitting surface in unit time is $\beta n\theta^{\frac{1}{2}}$, where β is a constant which may be calculated from the kinetic theory of gases. In general some of these will be reflected. Let the proportion absorbed be α . Then

$$N = \alpha\beta n\theta^{\frac{1}{2}} = \alpha\theta^{\frac{1}{2}} A\beta e^{\frac{1}{2} \int \frac{w}{R\theta^2} d\theta} \quad . \quad . \quad . \quad . \quad (54)$$

Thus for all values of θ

$$\frac{c}{4} \int \epsilon F(\nu\theta) E(\nu) d\nu = \alpha\theta^{\frac{1}{2}} A\beta e^{\frac{1}{2} \int \frac{w}{R\theta^2} d\theta} \quad . \quad . \quad . \quad (55)$$

According to Wien's law (p. 47)

$$E(\nu) d\nu = \nu^3 \psi\left(\frac{\nu}{\theta}\right) d\nu. \quad . \quad . \quad . \quad . \quad (56)$$

If experiments at low temperatures may be taken as a guide, $\epsilon F(\nu\theta)$ is independent of θ , so that we may expand this function as a series of powers of $\nu^{\pm\frac{1}{2}}$. By comparing the coefficients of the powers of θ with those of the expansion of the exponential on the right-hand side, the undetermined coefficients may be evaluated. In this way I find, putting $\frac{\partial w}{\partial \theta} = \frac{3}{2} R$ in accordance with § 3,

$$\epsilon F(\nu) = \frac{4}{c} \frac{\alpha\beta}{\nu^2} A \sum_{n=0}^{n=\infty} \frac{(-1)^n}{n!} \int_0^\infty \psi(x) x^{-n+1} dx \left(\frac{w}{R\nu}\right)^n. \quad (57)$$

The integrals in (57) are not mere numbers, since, according

to the radiation formulæ of Planck and Wien, they contain a parameter $\frac{h}{R}$, where h is Planck's constant. By changing the variable to $z = \frac{h}{R}x$, one finds

$$\epsilon F(\nu) = \frac{c^2 A \alpha \beta}{2\pi} \frac{h}{R^2 \nu^2} \sum_{n=0}^{n=\infty} \frac{(-1)^n}{n!} \int_0^\infty z^{1-n} \chi(z) dz \left(\frac{\omega_0}{\nu h}\right)^n, \quad (58)$$

where ω_0 is the part of ω which is independent of θ .

The integrals are now pure numbers, $\chi(z)$ being a function of z only. For example, if Planck's formula is used, $\chi(z) = (e^z - 1)^{-1}$. This solution shows that, provided the series exists and is convergent, and provided the results are not seriously affected by the somewhat arbitrary physical assumptions made, as to the independence of $\epsilon F(\nu)$ and θ , and so on, then $\frac{\nu^2 \epsilon F(\nu)}{\alpha A}$ is the same function of $\frac{\omega_0}{\nu h}$ for all substances. Thus, if we knew the variation of the photoelectric emission from any one substance, with the frequency of the light in the complete radiation, we should be able to construct the emission from any other substance from a knowledge of their respective values of w_0 . Since w_0 is smaller the more electropositive the metal, we should expect the emission to be excited by longer waves as the metals become more electropositive. This is, of course, in agreement with known experimental evidence. Somewhat similar properties hold for the mean kinetic energy of the electrons emitted by light of given frequency. I hope to be able to discuss these questions later, in connexion with new experimental results.

We have as the result of experiment some information about the form of $\epsilon F(\nu)$. We know that it is zero for small values of ν , and it may for most substances in all probability be put equal to zero over the part of the spectrum for which the formula

$$E\nu = \frac{8\pi}{c^3} h\nu^3 e^{-h\nu/R\theta} \quad . \quad . \quad . \quad . \quad . \quad (59)$$

is not a sufficiently accurate representation of the facts. This amounts to ignoring the part of integrals like that on the left-hand side of (55) contributed by the long wavelengths. A theory of photoelectric emission, based on the discrete theory of light, has been proposed by Einstein*.

* *Ann. der Phys.* xvii. p. 146 (1905).

According to Einstein the energy communicated to an electron by light of frequency ν is $h\nu$, where h , as also the h of equation (59), is Planck's constant. Part of this is used up in doing work P necessary to escape from the substance, the remainder forms part of the kinetic energy of the electron after it has escaped. Let us see to what extent the consequences of this type of theory are consistent with the conditions of statistical equilibrium.

To simplify the calculations we shall suppose that the work P is equal to the heat developed within the substance by the escaping electrons. This enables us to identify P with the w in (54). We shall also suppose that the reflexion coefficient of the electrons returned to the surface is independent of temperature. The properties deduced may therefore only be strictly true for an ideal body which absorbs all the electrons that fall on it. If we work out the value of β we find that

$$N = \alpha n \sqrt{\frac{R\theta}{2m\pi}} = \alpha \left(\frac{R}{2m\pi} \right)^{\frac{1}{2}} A \theta^{\frac{1}{2}} e^{\int \frac{w}{R\theta^2} d\theta}, \quad (60)$$

and in a similar way the kinetic energy E carried away from unit area of the surface in unit time is

$$E = \alpha n \left(\frac{2R^3}{m\pi} \right)^{\frac{1}{2}} \theta^{\frac{3}{2}} = \alpha \left(\frac{2R^3}{m\pi} \right)^{\frac{1}{2}} A \theta^{\frac{3}{2}} e^{\int \frac{w}{R\theta^2} d\theta}. \quad (61)$$

We also have by the substitution of (59) in (53)

$$N = 2\pi/c^2 \int_0^\infty d\nu \epsilon F(\nu) h\nu^3 e^{-\frac{h}{R\theta}\nu} \dots \dots (62)$$

Now, subject to the assumptions $P \equiv w$ and α is independent of θ , equations (60) (61) and (62) are not consistent with Einstein's suggestion that the whole of the energy of the emitted electrons arises from the energy $h\nu$ of a light unit. Let us see if they are consistent with a fraction γ of it arising in this way. If the energy given to each electron is $h\nu$ the part of the kinetic energy of each electron *which escapes*, which arises from this cause, will be $h\nu - w$, so that

$$\begin{aligned} \gamma E &= \frac{2\pi}{c^2} \int_0^\infty (h\nu - w) \epsilon F(\nu) h\nu^3 e^{-\frac{h}{R\theta}\nu} d\nu \\ &= \frac{2\pi h}{c^2} \int_0^\infty \nu \epsilon F(\nu) h\nu^3 e^{-\frac{h}{R\theta}\nu} d\nu - Nw. \quad (63) \end{aligned}$$

Differentiating (62) by θ on the assumption that the variation, if any, of $\epsilon F(\nu)$ with θ can be neglected, one finds

$$\frac{\partial N}{\partial \theta} = \frac{1}{R\theta^2}(\gamma E + wN). \quad . \quad . \quad . \quad (64)$$

Differentiating (60) by θ assuming α constant gives

$$\frac{\partial N}{\partial \theta} = \frac{1}{R\theta^2} \left\{ \frac{E}{4} + Nw \right\}, \quad . \quad . \quad . \quad (65)$$

whence $\gamma = \frac{1}{4}$. Since $E = 2NR\theta$ this might be interpreted by saying that on the average the light communicates to the escaping electrons an amount of energy equal to that belonging to each of the degrees of freedom.

The above result depends on the identification of P with w . P might be expected to be the same as w if the electrons expelled by photoelectric action have the full kinetic energy corresponding to the temperature of the metal before they are acted on by the light. This would be the case if the electrons which are subject to photoelectric action are free electrons or electrons which can become free, or, in fact, any electrons which contribute their share to the specific heat of the substance.

It is, however, possible that the photoelectrically active electrons are devoid of kinetic energy when inside the metal, and I am not convinced that such an event would necessarily involve a violation of the second law of thermodynamics. I mean, of course, in the way in which the phenomena of radioactivity may, loosely speaking, be said to violate the law. In that case the proper assumption would be $P = w - \frac{3}{2}R\theta$, $\frac{3}{2}R\theta$ representing the kinetic energy of the escaped particles. We should then have $\gamma = 1$ and the whole energy of the photoelectric electrons would come from the light. According to the results of § 3, the same conclusion would follow if P were identified with $w - \theta \frac{\partial w}{\partial \theta}$, an inter-

pretation which might be justified by thermodynamic considerations. The results would then be in accordance with what, as I understand it, is Einstein's position. In any event, it is clear that the view according to which the energy communicated to the electrons by light of a given frequency ν is equal to $h\nu$ and that a constant amount P of this energy is used up before the electrons can escape, is one which is consistent with the equilibrium conditions interpreted in the light of our present experimental knowledge of photoelectric phenomena.

The foregoing discussion has been restricted to the case of a body which is photoelectrically active but devoid of thermionic emission. We shall now consider the limitations which have been thus introduced. If we consider the atmosphere of electrons close to a flat face of the enclosure and a long way distant from the rest of the boundary, the electrons present will in general have come from a number of different sources. These are: (1) the stream from the interior of the cavity; (2) those of the incident electrons which are reflected at the interface; (3) those due to thermionic emission; and (4) those due to photoelectric action. The distribution of velocity among the totality of these four groups of electrons must be in accordance with Maxwell's law. The same is true of groups (1) and (3) individually, and must therefore be true of the sum of groups (2) and (4). We have seen in § 4 that the reflected group have Maxwell's distribution in the case of matter devoid of photoelectric action, and a similar argument may be used to demonstrate the same property for the photoelectric group when the material does not reflect any of the incident electrons but may emit thermionically. If the acts of reflexion and photoelectric emission are dynamically independent, it follows that (2) and (4) as well as (1) and (3) will each have Maxwell's distribution. It is probable that the two acts are almost independent even if they are not strictly so: in which case each group would have a distribution only differing slightly from Maxwell's. Although I have not been able to prove it, I think it probable that Maxwell's law will hold true for each individual group in every case. Thus, to sum up, we conclude that the results of the above theorems which have been deduced for an ideal body devoid of thermionic emission will, in any event, be nearly true and, in all probability, be exactly true for real bodies.

The foregoing considerations lead to a set of theorems relating to the functions which determine the distribution of velocity among the electrons emitted by the photoelectric effect which are similar to those given in § 4 for the reflected electrons. They may be expressed in the following fashion:—

The æthereal energy of frequency between ν and $\nu + d\nu$ which is incident on unit area in unit time at an altitude between θ and $\theta + d\theta$ and an azimuth between ϕ and $\phi + d\phi$ is

$$\frac{c}{4\pi} \sin \theta \cos \theta d\theta d\phi E(\nu) d\nu,$$

when all planes of polarization are included. As the radiation

is completely specified by $\theta\phi\nu$ and its two components polarized in two mutually perpendicular planes, the amount incident as above but polarized either in the plane of incidence or the perpendicular plane is

$$\frac{c}{8\pi} \sin \theta \cos \theta d\theta d\phi E(\nu) d\nu. \quad . \quad . \quad . \quad (66)$$

The amount absorbed in unit time is

$$\frac{c}{8\pi} \sin \theta \cos \theta d\theta d\phi (\epsilon_1(\nu\theta) \text{ or } \epsilon_2(\nu\theta)) E(\nu) d\nu,$$

where $\epsilon_1(\nu\theta)$ is the emissivity for radiation polarized in the plane of incidence, and $\epsilon_2(\nu\theta)$ the corresponding quantity for the perpendicular plane of polarization. $\epsilon_1(\nu\theta)$ and $\epsilon_2(\nu\theta)$ are functions of ν and θ and also of the temperature $T = (2kR)^{-1}$. Let $F_1(\nu\theta)$ and $F_2(\nu\theta)$ be the numbers of electrons emitted when unit quantity of æthereal energy specified by $\nu\theta$ and the respective planes of polarization is absorbed, the temperature of the material being $(2kR)^{-1}$. Let the respective proportions of these which have velocity components between u and $u + du$ be $f_1(\nu.\theta.u.v.w.k)du$ and $f_2(\nu.\theta.u.v.w.k)du$, the corresponding quantities for the perpendicular components being denoted by $g_1(\quad)dv$, $g_2(\quad)dv$, $h_1(\quad)dw$, and $h_2(\quad)dw$. The number of electrons having velocity components between u and $u + du$ which are emitted from unit area per second under the influence of the complete æthereal (black body) radiation may therefore be written

$$du \int_0^{\pi/2} \int_0^{2\pi} \int_0^\infty \sin \theta \cos \theta E\nu \{ \epsilon_1(\nu\theta) F_1(\nu\theta) f_1(\nu.\theta.u.v.w.k) \\ + \epsilon_2(\nu\theta) F_2(\nu\theta) f_2(\nu.\theta.u.v.w.k) \} d\theta d\phi d\nu. \quad . \quad (67)$$

The expressions for the numbers emitted with velocity components between v and $v + dv$ and w and $w + dw$ respectively are obtained by replacing $f_1 du$ and $f_2 du$ by $g_1 dv$ and $g_2 dv$ in the first case and $h_1 dw$ and $h_2 dw$ in the second. But as the distribution of velocity among all the electrons emitted under the influence of the complete radiation is to be in accordance with Maxwell's law, we have as an alternative expression for the number emitted with velocity components

between u and $u + du$

$$du \cdot 2kmv e^{-kmu^2} \int_0^{\pi/2} \int_0^{2\pi} \int_0^\infty \sin \theta \cos \theta E_v \{ \epsilon_1(\nu\theta) F_1(\nu\theta) \\ + \epsilon_2(\nu\theta) F_2(\nu\theta) \} d\theta d\phi dv. \dots (68)$$

The corresponding expressions for the v and w components are obtained if the factor outside the integral in (68) is replaced by $\left(\frac{km}{\pi}\right)^{\frac{1}{2}} e^{-kmv^2} dv$ in the first case and $\left(\frac{km}{\pi}\right)^{\frac{1}{2}} e^{-kmw^2} dw$ in the second.

Thus the functions $f_1 f_2$ have to satisfy the equation

$$\int_0^\pi \int_0^{2\pi} \int_0^\infty \sin \theta \cos \theta E_v \{ \epsilon_1(\nu\theta) F_1(\nu\theta) (f_1(\nu.\theta.u.v.w.k) - 2kmue^{-kmu^2}) \\ + \epsilon_2(\nu\theta) F_2(\nu\theta) (f_2(\nu.\theta.u.v.w.k) - 2kmue^{-kmu^2}) \} d\theta d\phi dv = 0. (69)$$

The corresponding equations for $g_1 g_2$ and $h_1 h_2$ are obtained if $f_1 f_2$ and $2kmue^{-kmu^2}$ are changed to $g_1 g_2$ and $\left(\frac{km}{\pi}\right)^{\frac{1}{2}} e^{-kmv^2}$ in the first case, and to $h_1 h_2$ and $\left(\frac{km}{\pi}\right)^{\frac{1}{2}} e^{-kmw^2}$ in the second.

These equations are true for all values of u, v, w , and k .

The obvious solutions $f_1 = f_2 = 2kmue^{-kmu^2}$ and so on do not accord with the experimental evidence, but there is no reason why they should be the only solutions.

It is perhaps necessary to point out that these deductions about photoelectric action are only valid for such phenomena as would go on indefinitely in an isolated enclosure. It is necessary, either that photoelectric fatigue should approach a limit, or that it should be due to other causes than the mere action of the light on the material. The experimental evidence seems to favour the latter hypothesis.

It will be noticed that the preceding conclusions about contact electromotive force and thermoelectric phenomena remain unaltered when the effects arising from æthereal radiation and photoelectric action are included. The difficulties introduced by the presence of the æthereal radiation may be avoided by carrying out the operations by using transparent pistons working in chambers lined with the same ideal transparent material.

Palmer Physical Laboratory,
Princeton, N.J.

LII. *The Electrochemistry of Radioactive Bodies.*

By GEORG VON HEVESY, *Ph.D.**

1. *Introduction.*

IT is well known that all metals when immersed in a liquid possess a tendency to go into solution. Each has a certain definite solution-tension, just as each liquid possesses a certain vapour-pressure. On these two conceptions Nernst has founded his theory of the origin of the electric current in a galvanic cell. Only in special cases, namely, with the very positive metals, is it possible to demonstrate experimentally the solution of a metal in water, because the excessively small amount of ions which the less positive metals produce in solution soon produces a sufficiently great osmotic pressure to prevent further solution of the metal.

The amount of some radioactive bodies necessary for detection is extraordinarily small compared with that of an ordinary chemical substance, and it is therefore to be expected that when a radioactive element is immersed in water, or in an aqueous solution, the ions thereby produced are capable of detection by these activities. Electrolytic decomposition of salt solutions, and the solution of the metals causing it, always accompanying each other, the smallest E.M.F. between two electrodes suffices to produce some decomposition of the salt, yet, as a rule, the solution-tension of the infinitely small amount of metal deposited on the electrode is sufficient to hinder further decomposition.

Continuous decomposition of a salt solution takes place only after a certain E.M.F. has been attained, viz. the decomposition voltage. This is the fundamental idea of Le Blanc's theory of decomposition. With solutions of radioactive bodies, however, it is to be expected that electrolytic dissociation is capable of being detected when the E.M.F. is less than the decomposition voltage.

The electrochemistry of radioactive bodies is thus not confined, as the electrochemistry of non-radioactive bodies is, to E.M.F.'s exceeding the decomposition voltage, but may deal with quantities of substances which are separated out by residual currents.

On the other hand, it must not be concluded in the case of radioactive bodies that because detectable amounts have been deposited by electrolysis on the electrode, therefore the

* Communicated by Prof. E. Rutherford, F.R.S.

decomposition voltage of the system under consideration has been reached.

When the magnitude of the decomposition voltage of a radioactive metal is known, its position in the series of electrochemical potentials can be determined, and thereby light may be thrown on its chemical nature. This is important, because the purely chemical properties of the shorter-lived radioactive bodies are so far only imperfectly known, owing to the minute quantities with which we are compelled to work.

Experiments have already been undertaken by v. Lerch on the separation of radioactive bodies electrochemically in order to determine their places in the series of electrochemical potentials *. One of the methods of electrolysis he made use of in this work consisted in dipping a plate of metal in a salt solution containing radioactive matter to bring about its deposition on the plate. This process is a local galvanic action.

Just as copper is assigned a place in the series of potentials between iron and silver, because it is capable of being deposited on an iron plate but not in detectable amount on a silver plate, so radium C was placed between nickel and silver, because it is deposited on the former but not on the latter. This conclusion, however, is not of itself justifiable if the considerations discussed above are admitted. They would rather lead us to expect that *every metal is capable of causing the deposition of every radioactive body to a greater or a less degree*, but never in amount less than can be detected by the methods of radioactivity.

This the author has succeeded in showing experimentally. Every radioactive body dealt with—viz. radium, radium A, radium B, radium C₁, radium C₂, radium D, radium E, and radium F; thorium X, thorium B, thorium C, and thorium D; actinium B, actinium C, and actinium D—is capable of being deposited on all metals, not excepting even gold and silver. The experiments have been carried out in neutral solutions; for in acid solutions, with which previous experimenters have for the most part worked, disturbances to the results of electrolysis arise from the solution of the deposited body in the acid.

An account will be published in a later communication of the amounts of the various products obtained under different conditions by electrolysis, and also the arrangement of the radioactive bodies according to their potentials. This series

* v. Lerch, *Ann. d. Physik*, xii, p. 766 (1903); *Jahrb. der Radioakt.* ii. p. 471 (1905).

is connected with the series of potentials of ordinary metals by a knowledge of the potential of radium, for this body can obviously be investigated either as a radioactive body or as a purely chemical substance.

In this paper the influence of the electrode potential on the electrolytic separation of the active deposits of radium, thorium, and actinium is discussed.

2. *The Function of the Electrode Potential.*

Various electrode potentials can be obtained by dipping in the solution under examination a pair of electrodes not acted on by the liquid, and applying varying E.M.F.'s. By this method, however, it is difficult to obtain definite E.M.F.'s, on account of the conductivity of the solution and its change with polarization at the electrode. For this reason, another method was used in which the electrolysis was carried out, not by applying a difference of potential between the electrodes, but simply by dipping the metal into a solution of one of its salts containing the radioactive body under investigation.

For instance, the action of zinc on the active deposit of radium was investigated by dipping a zinc plate into a solution of zinc sulphate containing radium B and radium C. This is analogous to producing the deposition of copper on an iron plate by dipping it into a solution of FeSO_4 and CuSO_4 . In the latter case, however, the potential difference Fe/FeSO_4 gradually falls to that of Cu/CuSO_4 , owing to the increasing deposition of copper on the iron plate. On the other hand, however, the deposition of about 10^{-17} grm. of RaC cannot influence the potential difference Zn/ZnSO_4 , the zinc acting electrochemically throughout as pure zinc.

The potential differences used are summarized in the table that follows. Their values are taken from the latest work on galvanic cells*.

All electrolytes may be used in this work with the exception of acids and of solutions of such bodies as the salts of zinc and bismuth, which tend to become turbid. The former class are not suitable for use, owing to their action on the matter deposited on the electrode; while in a turbid solution the radioactive bodies are apt to be precipitated.

The values of the single potential differences measured against the normal calomel electrode are given in the following table:—

* "Messungen electromotorischer Kräfte," *Abhandlungen der Bunsen Gesellschaft*, n. 5 (1911).

	$\epsilon_{(\text{Hg})}$ in volts.
Ag/AgNO_3 1 mol.	+0.49.
Ag/AgNO_3 0.1 mol.	+0.43.
Ag/AgNO_3 0.01 mol.	+0.37.
Cu/CuSO_4 0.5 mol.	+0.02.
$\text{Cu}/\text{CuSO}_4 + \text{Na}_2\text{SO}_4$ 0.05 mol. 0.05 mol.	-0.02.
$\text{Ag}/\text{AgBr}, \text{KBr}^*$ Solid. 0.1 mol.	-0.15.
$\text{Pb}/\text{Pb}(\text{NO}_3)_2$ 0.5 mol.	-0.43.
$\text{Pb}/\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ 0.5 mol.	-0.47.
$\text{Pb}/\text{Pb}(\text{NO}_3)_2 + \text{NaNO}_3$ 0.05 mol. 1 mol.	-0.48.
$\text{Pb}/\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{NaC}_2\text{H}_3\text{O}_2$	-0.58.
$\text{Ag}/\text{Ag}(\text{CN})_2 + \text{KCN}$.	$-0.72 + 0.06 \log \frac{\text{Ag}(\text{CN})_2'}{(\text{CN}')_2}$.
Cd/CdSO_4 0.5 mol.	-0.71.
$\text{Cd}/\text{CdSO}_4 + \text{Na}_2\text{SO}_4$ 0.005 mol. 0.5 mol.	-0.78.
$\text{Au}/\text{Au}(\text{CN})_2 + \text{KCN}$.	$-0.88 + 0.06 \log \frac{\text{Au}(\text{CN})_2'}{(\text{CN}')_2}$.
Zn/ZnSO_4 0.05 mol.	-1.1.
$\text{Zn}/\text{Zn}(\text{CN}) + \text{KCN}^\dagger$ 0.025 mol. 0.25 mol.	-1.5.
Mg/MgSO_4 0.5 mol.	-1.9.

* AgBr must be added to the KBr in the solid form; for if it is made by precipitation in the solution, the greater part of the radium C is precipitated with it.

† Varying amounts.

The radioactive substances whose properties are discussed in this paper are included in the three active deposits of radium, thorium, and actinium. The radiations emitted, and the half-value periods of transformation of the constituent products, are shown in the table below. The nomenclature is that given by Rutherford and Geiger, *Phil. Mag.* Oct. 1911, p. 621.

Substance.	Radiation.	Period.
Radium A	α	3.0 minutes.
„ B	β, γ	26.8 minutes.
„ C	α, β, γ	19.5 minutes.
Thorium A	α	.14 second.
„ B	β	10.6 hours.
„ C	α	55 minutes.
Actinium A	α	.002 second.
„ B	β	36 minutes.
„ C	α	2.15 minutes.

It will be seen that there is a remarkable similarity between the nature of the radiations from the corresponding products. It will also be shown that there is a corresponding similarity in their electrochemical properties. It is consequently very convenient to speak of the B or C products, meaning in the former case radium B, thorium B, and actinium B, and in the latter case radium C, thorium C, and actinium C.

An active deposit was obtained in the usual way on a platinum electrode, and then dissolved in HCl, HNO₃, or H₂SO₄, according to requirement, and evaporated to dryness. It was then treated with distilled water, and as soon as a B product was in equilibrium with a C product an electrolyte was added to it. If, for instance, the action of zinc on the radium active deposit was being investigated, the active deposit was dissolved in H₂SO₄, and the (RaB)_x₁(SO₄)_y₁ + (RaC)_x₂(SO₄)_y₂ solution evaporated to dryness, redissolved, and added to a solution of zinc sulphate.

In some experiments the active deposit was collected on the surface of metallic sodium, which was then dissolved in water, the active deposit dissolving also. This second method

is of great value in the investigation of a very short-lived body such as radium A, for electrolysis may be begun as soon as the sodium commences to dissolve.

The volume of liquid used in the experiments to be described was always 8 c.cm. The surface of the electrode was 2.5 sq. cm., and one side was coated with enamel. The electrode was always rotated evenly in the liquid for a definite interval. The time of immersion was four minutes in the experiments on the radium and thorium active deposits, and two minutes for those on the actinium deposit. When this time had expired, the electrode was immediately washed with distilled water, dried with filter-paper and inserted in the α -ray electroscope, and its change of activity measured for a considerable time. In all the experiments activity was measured by α -rays only. The absolute amount of RaC in the solutions used varied between

$8 \cdot 10^{-16}$ and $4 \cdot 10^{-16}$ gr. per c.cm. of solution, and of ThC,
 $1 \cdot 10^{-16}$ and $0.5 \cdot 10^{-16}$ gr. per c.cm. of solution.

These figures are obtained by calibrating the electroscope with a U_3O_8 film emitting a known number of α particles. For the film I am indebted to Dr. H. Geiger. The calculations involve the known periods of thorium, radium, radium C, and thorium C, the number of α particles emitted by these elements (Rutherford and Geiger), and the ranges of the α particles of uranium, radium C, and of thorium C. If, in addition, the branching in the thorium series be taken into account, the concentration of thorium C becomes three times less. (*Cf.* paragraph 10.)

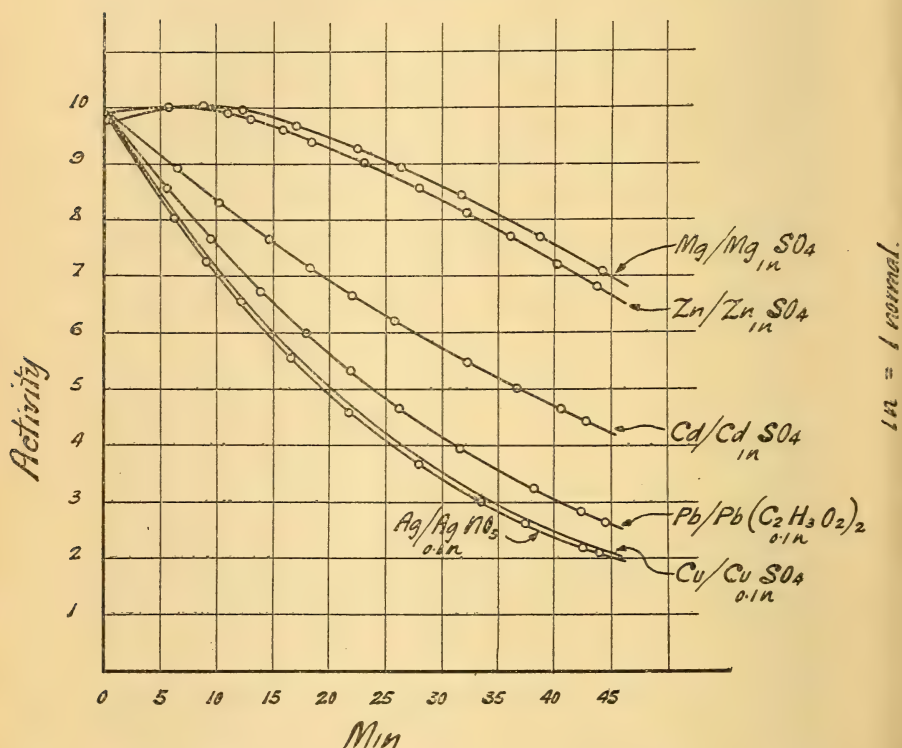
3. *The Ratio of the amount of B product to C in the Radium, the Thorium, and the Actinium Series, as Functions of the Electrode Potential.*

With a positive potential like that of silver the deposit on the electrode is practically pure C. If we proceed from silver to zinc, the potentials becoming less and less positive, the ratio of the amount of C to that of B separated out diminishes continuously, until when negative potentials are reached B is deposited in excess of C. This is shown by the curves obtained. As the potentials become less positive, the curves which at first are decay-curves of C gradually become less steep, until a potential is reached at which B and C separate out in equilibrium amount. With more negative potentials the curves become rise-curves, owing to the excess of B over C.

Several of the curves obtained for radium, thorium, and actinium products, typical of a great number (over 100), are shown in figs. 1, 2, and 3.

Fig. 1.

Rd B + Rd C.



From the variation of the activities in the series of curves given, it is not difficult to deduce the relative amounts of B and C products which have been deposited. For example, to one who is acquainted with the nature of the decay-curves, it is obvious that the two upper curves of fig. 1 show at once that radium B is in excess of the equilibrium amount, and that the four lower ones indicate that B is present in less than equilibrium amount.

The curves corresponding to any one potential are capable of being repeated with great exactness, except in the case of magnesium, which gives inconstant results owing to the evolution of hydrogen at its surface. In the figure the steepest rise-curve obtained is given.

Fig. 2.

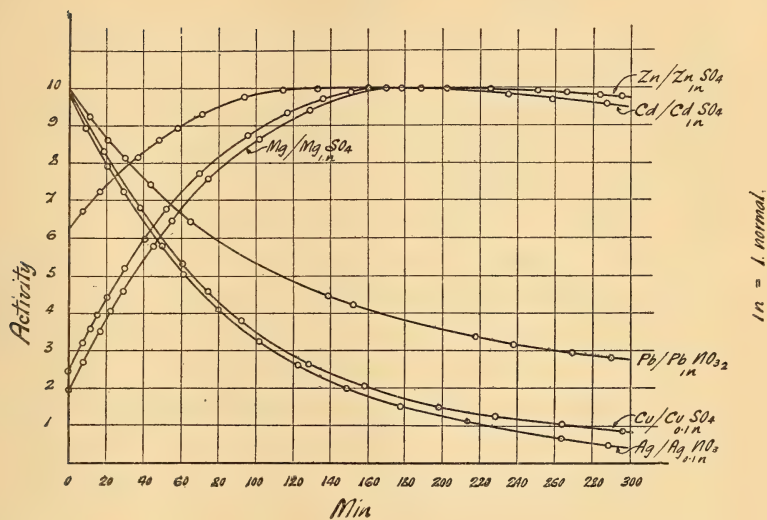
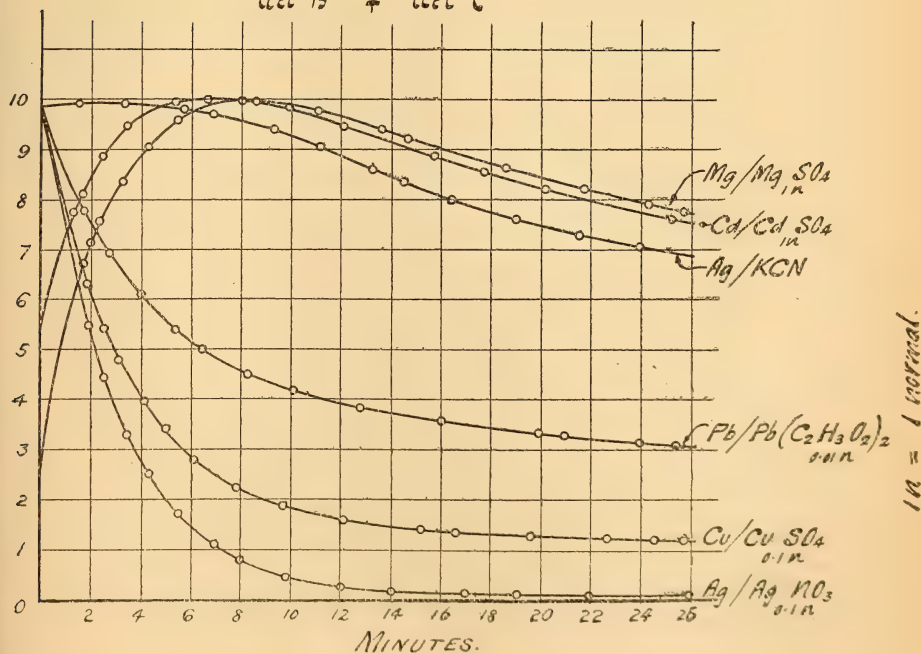
 $Th\ B + Th\ C$ 

Fig. 3.

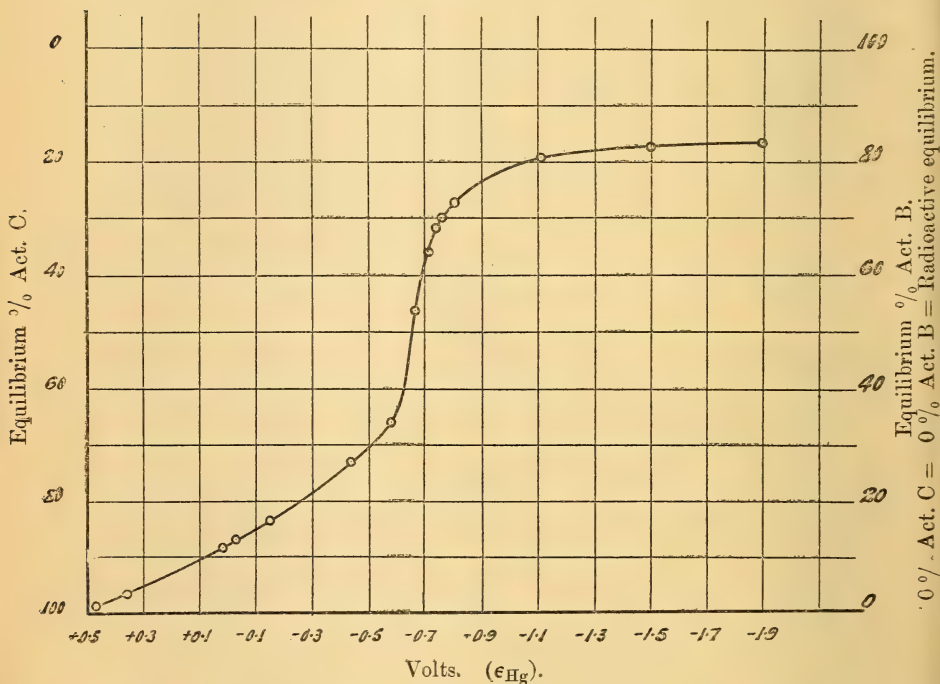
 $Act\ B + Act\ C$ 

In this work the period of thorium C has been taken, not as 55 minutes, as is usually done, but in accordance with v. Lerch's measurements (*loc. cit.*) as 60.5 minutes.

The curves obtained, and the results deduced from them, show that the three B products appear to be identical in their electrochemical behaviour, and the three C products also.

Figs. 4 and 5 show the relationship between the percentage of C and B respectively of the total amount deposited on the electrode, and the potential required to bring about deposition.

Fig. 4.

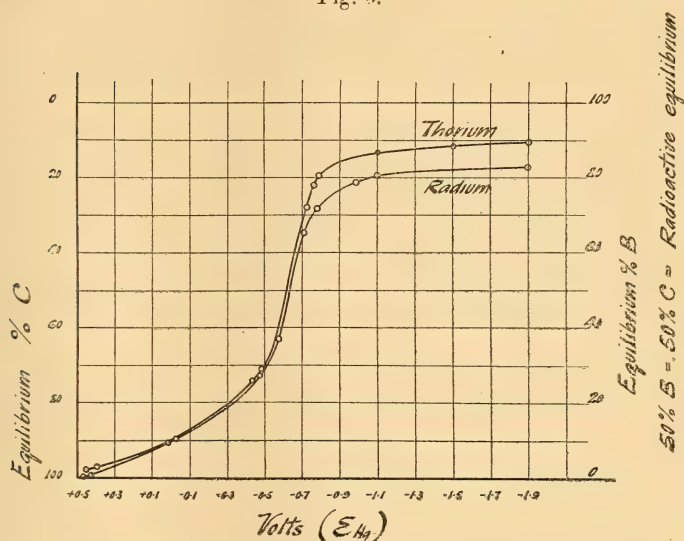


"Percentage" means the percentage of the equilibrium amounts, 50 per cent. representing a deposit of B and C in amount corresponding to radioactive equilibrium.

The potentials, of course, are measured against the calomel electrode. It is seen that the curves in all three cases are remarkably analogous. It would be natural to expect that very pure C could be obtained with the potentials $\text{Au}/\text{H}_2\text{AuCl}_6$ or $\text{Pt}/\text{H}_2\text{PtCl}_6$. This is, however, not so, for in these cases gold acts like a metal lying between silver and

copper. The E.M.F.'s between gold or platinum and their solutions are hardly comparable with those tabulated above,

Fig. 5.



for the ions of the metals in these two cases are present as complex anions. A further complication arises from the so-called air-potential.

4. The Function of the Salt Solution in the Electrolysis.

Electrochemically definite systems.

According to Nernst's theory, the single potential difference at any electrode is given by the expression

$$E = RT \log \frac{P}{p},$$

where P is the so-called solution-tension of a metal, a constant characteristic of it, and p the osmotic pressure of the ions of the metal present in the liquid surrounding the electrode. p is proportional to the concentration of these ions, and therefore the above expression may be written

$$E = RT \log \frac{C}{c} \text{ where } C \text{ is a new constant.}$$

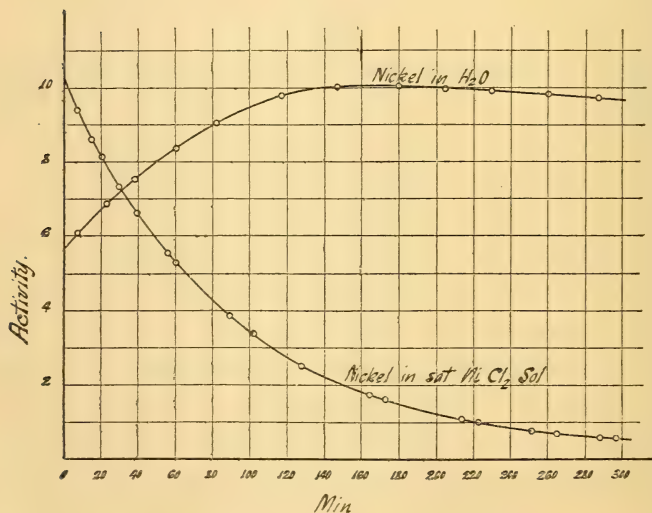
The difference of potential between a metal and an electrolyte depends, therefore, on the concentration of the ions of the metal. The case when $c=0$ and therefore E infinite cannot be realized; on the contrary, dipping a metal into

water results in an immediate production of some ions at the surface separating them and E assumes a finite value. This variation of potential difference is a phenomenon depending on many factors, and we can, therefore, have definite potential differences between a metal and an electrolyte, only when the latter contains a known quantity of a salt of the former.

One of the chief causes of the elucidation of the relationship mentioned in the last paragraph between the E. M. F. Metal/Electrolyte, and the composition of the mixture of B and C deposited, was the fact that in every case only electrochemically definite systems were employed. In what follows, a definite system will be used to denote a system in which an electrode dips into a solution of one of its salts, an indefinite system, one in which a metal dips into any other liquid.

Fig. 6 shows the difference between an indefinite potential difference, *e.g.*, Nickel/water, and a definite one

Fig. 6.

Th B + Th C.

Nickel/NiCl₂. In the former case a rise-curve is obtained (denoting excess of B over C), corresponding to a negative potential difference Metal/indefinite Electrolyte, and in the latter case, a decay-curve (C present practically in the pure state). These differences are complicated in the case of nickel owing to its passivity, which causes it to act as

though it had a different potential from that which it really has, but in the case of copper they are well marked.

The indefinite potential difference $\text{Cu}/\text{H}_2\text{O}$, when the copper is dipped in water exactly a minute, is the same as that between cadmium and cadmium sulphate, *i.e.*, 0.7 volt more negative than the definite potential of copper, for B and C are deposited on the copper in the same ratio as on cadmium.

Again, silver dipping into a solution containing Cl' ions has the same potential as the definite potential of copper, and when it dips into a KCN solution, it shows the potential of cadmium. It is, therefore, obvious that such expressions as "deposited on copper, not deposited on silver," &c., are quite indefinite, and it is from this indefiniteness that contradictory assertions regarding the deposition of radioactive bodies on certain metals have arisen.

5. *Further evidence that the Potential of the Electrode determines the composition of the mixture of B and C.*

If an acid solution containing B and C in equilibrium be electrolysed with a very small current density (a fraction of a milliampere per sq. cm.), with platinum electrodes, *i.e.*, with a voltage very much below the decomposition voltage of water, very pure radium C is obtained*.

The fact that the decomposition voltage has not been reached means simply that there is a smaller potential difference at the cathode than there is at the normal hydrogen electrode. The further we can keep below the potential difference at the hydrogen electrode the purer is the C obtained. If, next, the potential difference between the electrodes exceeds the decomposition voltage of water, and therefore at the cathode the potential difference is equal to that at the hydrogen electrode, a mixture of B and C is obtained of the same composition as was obtained with a potential difference of $\epsilon_{(\text{H}_2)} = -0.4$ volt by the first method.

If the electrolysis be carried out in a neutral, or better, in an alkali solution, a more negative potential difference is obtained at the hydrogen electrode ($\epsilon_{(\text{H}_2)} = -1.1$ volt) owing to the smaller concentration of H' ions in the solution. The mixture of B and C obtained in this case on the electrode is that obtained on cadmium in the first set of experiments ($\epsilon_{(\text{H}_2)} = -0.7$ volt), the B being in excess of the C. If, finally, the decomposition voltage of water is exceeded by

* For thorium C, v. Lerch (*Wien. Ber.* cxiv. 11a (1905); for actinium C, Miss Brooks, *Phil. Mag.* vol. viii. p. 373 (1904).

using a large current density, the mixture of B and C deposited in the cathode is similar to that obtained by the first method on zinc ($\epsilon_{(\text{Hg})} = -1.1$ volt).

In this way it is clearly shown that the composition of the mixture of B and C obtained on an electrode is purely a function of the potential difference.

6. *Previous work on Electrolysis of Solutions containing an Active Deposit, the explanation of v. Lerch's method of separating Radium C.*

Dorn was the first to carry out an electrolysis of radium solutions *. In 1903 v. Lerch † electrolysed an acid solution of thorium active deposit. A year later Miss Brooks ‡ electrolysed the HCl solution of the active deposit of actinium, and Pegram § a solution of thorium nitrate.

V. Lerch found later || that by dipping a nickel wire into a HCl solution of radium active deposit, extremely pure radium C could be obtained on it.

This convenient method of preparing pure radium C is known as v. Lerch's method, and became of great practical importance in later work.

The method may be explained thus :—

(1) The potential difference Nickel/Electrolyte is abnormally negative and is equal to that at the hydrogen electrode. This is due to the considerable resistance of the nickel ions—as contrasted with the behaviour of all other ions—in giving up their charge. On account of this phenomenon of Passivity the potential difference Nickel/Electrolyte is well suited for bringing about the deposition of radium C. The radium C thus deposited is not at first pure; the purification is due to the action of the acid.

(2) Deposition of a substance on an electrode and solution therefrom in an acid are contrary phenomena. Radium B is deposited on nickel much less easily than radium C; it is also much more easily soluble in the hot acid than radium C. Radium C has, therefore, a double chance of being deposited pure.

(3) If nickel be dipped into neutral solutions pure radium C is never deposited on it. The composition of the mixture of B and C varies with the passivity of the metal.

More than thirty experiments, for the most part with thorium B and C, have been carried out. The C content

* *Abh. der nat. Ges. Halle* (1900).

† *Ann. d. Phys.* xii. p. 745 (1903).

‡ *Phil. Mag.* Sept. 1904.

§ *Phys. Rev.* xvii. p. 427 (1903).

|| *Wien. Ber.* cxvi. IIa, Dec. 1907.

of the mixture deposited on the nickel varied from 90 to 50 per cent. of the equilibrium amount. These numbers correspond to potentials of from $\epsilon_{(\text{Hg})}=0$ to $\epsilon_{(\text{Hg})}=+0.6$ volt.

7. *Explanation of the Inflexion Curves.*

The curves of figs. 4 and 5 have inflexion points at approximately 50 per cent. of the equilibrium amount of C. This point corresponds to a potential difference of -0.63 volt measured against the calomel electrode.

If an electropositive metal, such as zinc, be dipped into a normal ZnSO_4 solution, the latter becomes charged positively and the zinc negatively owing to the passage of zinc ions into the solution. If an electronegative metal, however, such as silver be dipped in a normal AgNO_3 solution, the solution becomes negative, and the metal positive, because in this case positive ions are deposited on the metal. Again, if a metal be dipped in a solution of one of its salts and becomes charged neither positively or negatively, there is no potential difference between metal and electrolyte.

Experiments have been carried out with care to determine this absolute zero of electrolytic potential. They show that the value ($\epsilon_{(\text{Hg})}=+0.56$ V absolute), deduced from measurements with the dropping electrode, is only approximately correct. It is, however, quite definitely known that metals like zinc and cadmium are charged negatively with respect to normal solutions of their salts, and metals like copper and silver positively.

The question as to how far this point of inflexion is bound up with the absolute zero of potential is left an open one; the conclusion is drawn, however, from the shape of the inflexion curve that B tends to deposit on a negatively charged electrode, C on a positively charged one. Two other explanations, however, are possible. One is to assume that the curves of figs. 4 and 5 relate to decomposition voltages. As the potential increases, more and more of B separates out with the C, and after the decomposition voltage of the former is reached, both are deposited by electrolysis in the ratio of their concentrations. On this view, however, difficulties arise when we attempt to explain the part of the curve which lies above the point of inflexion, for it seems entirely anomalous for high potentials to bring about the electrolysis of electropositive metals to a greater extent than electronegative. If the valency of thorium C were much greater than that of thorium B, this difficulty would be removed, and the above explanation would become possible.

There is still another explanation possible, and that is to assume that in solution, in addition to the ions of B and of C which react with those of the immersed metal, there are also free ions present, which are drawn in to the double layers at the boundary of the metal and the solution. Free ions are such as can be separated from corresponding ions by diffusion. They are always present in electrolytes, but only to a very small extent; they differ quantitatively from colloidal particles only by their large value of e/m . This view receives some support from the experiments carried out on non-metals. If such bodies as glass, quartz, sulphur, &c., be dipped in an active solution, a mixture of B and C, containing chiefly C, is deposited on them though to a very much smaller extent than on metals.

That the smallest double layer which is always present at the surface of separation of two different phases is sufficient to produce deposition of a portion of the active matter on the solid phases, is shown very well by the behaviour of radium F; for radium F is not only extraordinarily easily deposited on a surface but is also extremely difficult to be removed from it.

To decide between these various explanations experiments have been commenced on the migration and the diffusion of the radioactive ions. When they are finished it is hoped that results bearing on the valency and the sign of the ions will be obtained.

8. *Determination of the Potential Difference between Metal and Electrolyte from the Electrochemical action of the former on radioactive substances.*

It has been shown that the ratio in which the B and C products of radium, of thorium, or of actinium, are deposited on metals immersed in solutions containing them, or on platinum electrodes in the ordinary course of electrolysis, is a function of the potential difference between metal and electrolyte. Conversely, from a knowledge of this relationship given by the results of figs. 4 and 5, the single potential difference Metal/Electrolyte can be obtained from the ratio of B to C in the active matter deposited on the metal. This method is especially valuable when it is necessary to determine this potential difference as rapidly as possible.

If actinium B and C be used as indicator, only a few α -ray measurements of the activity of the plate need be made, and after a few minutes an accurate value of the potential difference under investigation is obtained.

With thorium B and C, measurements of the activity curve cannot of course be completed so quickly as with actinium B and C, but on account of the slow variations of activity of the former, the experiments yield more accurate results.

Radium B and C is not at all suitable for these measurements, owing partly to the small difference in the periods of B and C (26.8 mins. and 19.5 mins. respectively), and partly because B and C come into equilibrium with each other only after a certain time has elapsed owing to the presence of radium A. With thorium and actinium bodies, equilibrium is immediately attained because of the excessively short periods of thorium A and actinium A.

The suitability of this method of measuring single potential differences has been tested by determining the potential of tantalum, which has hitherto been unknown. A plate of tantalum kindly supplied to me by Dr. W. v. Bolton, was immersed in a vessel containing normal potassium chloride for an hour; a solution of $\text{ActB}_{x_1}\text{Cl}_{y_1} + \text{ActC}_{x_2}\text{Cl}_{y_2}$ was then added to the chloride solution and the tantalum removed two minutes later.

The composition of the actinium products on the plate, calculated from the decay of its α activity, was practically the same as that deposited on a copper plate which has been dipped into a $\frac{1}{10}$ N. CuSO_4 solution. The potential difference Tantalum/KCl (normal) is, therefore, -0.03 V with respect to the calomel electrode.

Under identical conditions Mr. Slade and the author, measuring the potential by means of the usual electrical compensation method, found the value -0.04 V.

The agreement is remarkably good considering that the system under consideration is not "definite."

In another experiment the potential difference $\text{Ta}/\text{Ta}_2\text{O}_5$ solution gave by the radioactive method 0.00 V, and by the electrical method also 0.00 V.

9. *Change of Potential Difference between a Metal and a Solution with a change in the Ionic Concentration.*

If a metal be dipped in pure water, then since the latter contains no ions of the former, the potential difference between the two is really much greater than the potential difference between the same metal and a solution of one of its salts. With time it approaches a final value asymptotically. In other words, the potential difference changes as more and more of the ions of the metal are produced in the

solution. This process is demonstrated very clearly by the methods described in this paper, and some results will be given here, though a complete account is reserved for a subsequent communication. If a copper plate be dipped in water containing radium B and radium C in equilibrium for 0.2 sec., the mixture of B and C obtained on it contains more than 85 per cent. of B, and corresponds, therefore, to an E.M.F. of 2 volts measured against the calomel electrode. The electronegative metals, therefore, really commence to decompose water immediately after being dipped in it. If measurements of this process be observed for periods longer than a few seconds, the results are less concordant than those obtained with short exposures, and depend somewhat on the gases surrounding the plate (air, hydrogen, &c.). Here, also, oxidation of the copper, and solution of the oxide formed, play no inconsiderable part, processes which in the case of mercury have been investigated thoroughly by Warburg. However, the production of positive ions in the water seems always to take place much more rapidly than the second process of oxidation and solution of the oxide, and by working rapidly this second process may be entirely obviated.

10. *The Electrochemical behaviour of Thorium C and the branching in the Thorium Series.*

A consideration of the curves of figs. 4 and 5 shows at once that radium C can be separated in a much purer form by the method * described in this paper than either thorium C or actinium C. This can be explained as being due to small differences in the electrochemical properties of the three C's, or may be explained as follows :—

When radium B and C are present in equilibrium amounts, it follows from their periods that for every radium C molecule present there are 1.4 molecules of radium B. In the case of thorium B and C, this ratio is 10.6, and consequently the probability that some B will separate out with the C is much greater. In the case of actinium B and C, however, although the ratio of B molecules to C molecules is higher

* The method used by v. Lerch proves this also, for Fajans (*Phys. Zeit.* xii. p. 370 (1911)) using this method was able to obtain radium C containing less than 0.05 per cent. of radium B. From v. Lerch's work on thorium C (*Wien. Ber.* cxvi. p. 6 (1907)), however, it is found that the period of thorium C prepared by deposition on nickel is about 0.75 min. too high, on account of the presence of a little thorium B. This amount can be readily calculated from the data supplied, and is 1 per cent. of the equilibrium quantity of thorium B.

than the corresponding ratio for the thorium series, being 17, actinium C can be separated out in a much purer state than thorium C.

This apparent inconsistency can be explained most easily by assuming that the ratio of the number of thorium B molecules to the number of thorium C molecules in equilibrium, is not the same as the ratio of their periods, but greater.

Marsden and Barratt* found recently that there is a branch product in the thorium series. For every 100 atoms of thorium C emitting α -particles, 65 expel α -particles of range 8.6 cm. and 35 α -particles of range 4.8 cm.

If the former of these products be the product in the thorium series corresponding to radium C₁ and actinium C in the radium and actinium series respectively, then the ratio of the number of molecules of thorium B to that of thorium C is 16; if it be the latter, *i. e.*, the 35 per cent product, this ratio is 30.

If we assume that the 35 per cent. product is the body corresponding to radium C and actinium C, the anomaly found above disappears, since now the ratio thorium B to thorium C₁ being greater than the corresponding ratio for actinium, it is only to be expected that thorium C would be more difficult to separate out in the pure form than actinium C.

Summary.

1. The general electrochemical properties of radioactive bodies are discussed in this paper. It is shown that the deposition of these bodies on platinum electrodes in the ordinary course of electrolysis, or on a metal dipping into an active solution, depends to a large extent on the potential of the electrode.

2. Radium B, thorium B, and actinium B, possess the same electrochemical properties. Radium C, thorium C, and actinium C possess also the same electrochemical properties. With very small electrode potentials C is deposited almost pure; as the electrode potential is increased, the amount of B separated with the C increases also. When $\epsilon_{\text{H}_2} = -0.6$ V, B and C are deposited in equilibrium amount. With higher potentials chiefly B is obtained.

3. A relation exists between the E.M.F. Metal/Solution, and the ratio of B to C deposited on the metal dipping into the solution. When the latter is known, therefore, the former is also known. From this relation, the unknown

* Marsden & Barratt, Proc. Phys. Soc. vol. xxiv. p. 50 (1911).

position of tantalum in the series of potentials has been determined. By this method, also, the change of E.M.F. Metal/Water with time of immersion of the metal can be determined.

4. The results of Marsden and Barratt on the branching of the thorium series are consistent with the results obtained on the electrochemical behaviour of thorium C.

I have to express my thanks to Professor Rutherford for his help and advice throughout these experiments, and also for the radioactive material placed by him at my disposal.

Physical Laboratories,
The University, Manchester,
February 1912.

LIII. *On the Trisection of an Angle.*

By NEVIL MASKELYNE, *F.R.A.S.**

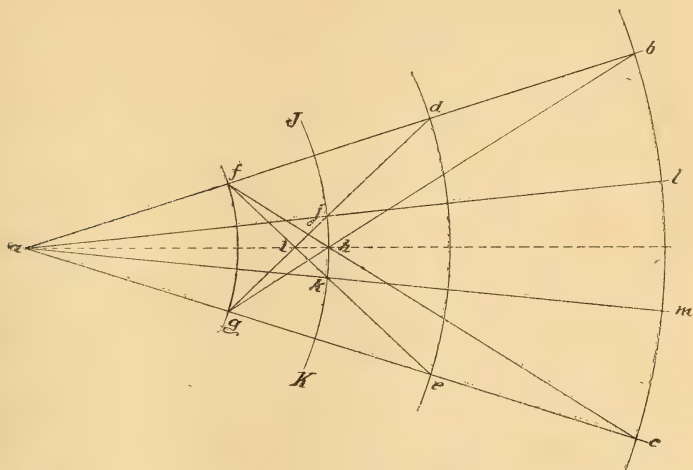
THE trisection of an angle, irrespective of its magnitude, by means of any geometrical construction, has been regarded as impossible. The problem has been associated with perpetual motion, the transmutation of metals, "zetetic" astronomy, and similar absurdities. Mathematicians have spoken in no measured terms of the folly displayed by those who, in the face of proved impossibility, attempt to provide a solution. In short, the subject has been relegated to the list of fallacies which are entertained only by very ignorant or very much misguided persons.

In the past, this view of the matter has given me some uneasiness. The reason being that at any moment, in the course of my everyday work, I might find myself called upon to solve this very problem. I cannot, however, say that the prospect troubled me greatly. Judging by experience, I felt confident that, when the difficulty arose, means for overcoming it would not be entirely lacking. Nevertheless I could not altogether set aside the adverse pronouncements made by eminent men, whose opinions and decisions compel the utmost respect, by virtue of authority.

Eventually, as I had long anticipated, it became necessary to devise some simple link-motion which would perform the function of trisecting a variable angle. That, necessarily, involved the discovery of some geometrical construction, by means of which any angle may be trisected. Reduced to

* Communicated by the Author.

geometrical form, the construction I have devised is represented in the accompanying diagram.



Take any angle bac and at regular distances from a describe the arcs fg , de , and bc , with a as centre. Join, respectively, the points bg , cf , dg , and ef . The line aih , of course, bisects the angle bac . With radius ah and a as centre, describe the arc JK , cutting dg and ef at j and k . The lines al and am , drawn respectively through j and k , trisect the angle bac .

St. George's Hall, W.,
Dec. 11, 1911.

LIV. *On the Direct or Indirect Nature of the Ionization
by X-rays.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN the February number of the *Philosophical Magazine* Dr. Barkla criticises some results obtained by Mr. Porter and myself. We had shown that all the ionization in oxygen due to X-rays could be ascribed to an indirect action of the rays, effected through β rays originated in the gas by the X-rays, provided that the ratio of the absorption coefficients of the X-rays in silver and in oxygen was about 34. According to our experiments the value of this ratio was 36.3; and we therefore looked upon our work as confirming the deduction—made previously as the result of an entirely different argument—that the action of X-rays was mainly, if not wholly,

indirect. Dr. Barkla says that we ought to have allowed more for the scattering of the X-rays by the screens of lower atomic weight, that if we had done so we should have found a value for the ratio nearly twice as great as that which is stated above, and therefore that we had not proved our point.

It is quite true that the screens of low atomic weight scatter the X-rays (in this case, Sn X-rays) to a considerable extent: but the silver screen also scatters the X-rays. Whether the process is exactly of the same nature is not of importance: experiment shows that the ratio of the absorption coefficients of silver and of (say) carbon is very little altered if the screens are placed close to the ionization chamber so that scattered rays enter it, or farther away so that they do not. If silver and carbon plates are used in turn as that wall of the ionization chamber on which the X-rays fall, the returned radiation is not very different in either quality or quantity. I think we were sufficiently correct in adopting the value 36.3, and in drawing our main conclusion.

Dr. Barkla would leave the question of the directness or indirectness of the ionization an open one, arguing that our experiments furnished no direct evidence in favour of the view to which they led us. I venture to think that this attitude is not strictly logical. When the passage of X-rays through a gas was first found to be accompanied by the ionization of the gas, it was assumed that the former process was the cause of the latter. This was the right thing to do; but when it appeared further that the X-rays produced β or cathode rays which were already known to possess ionizing powers, all evidence for the direct action disappeared. It became improper to assert the direct action until it had been shown that the newly discovered indirect action was insufficient; and such evidence, it seems to me, is still wanting.

Meanwhile, it appears from energy considerations which I have tried to state at various times, and which Dr. Barkla does not attack, that the X-rays cannot spend much energy in their flight, and that therefore they cannot have much ionizing action: unless, indeed, ionization can be accomplished without the expenditure of energy.

The experiments of Mr. Porter and myself were an attempt to show that an inference arrived at on other grounds was consistent with facts so far as they could be ascertained. I do not suppose that they supply a test of more than a ten per cent. accuracy: in an earlier paper of mine (Phil.

Mag. Sept. 1910) was a rougher estimate which Dr. Barkla criticises also. Two years earlier still I made attempts which were, I fear, even less accurate. But I hold that under the circumstances all these were right and proper.

The main part of Dr. Barkla's paper is concerned with experiments on the ionization of gaseous mixtures, and deductions therefrom. The latter may be summed up in three statements.

(1) Ionization by X-rays is not purely atomic. It depends to a certain extent on the chemical combinations in the molecule.

This is quite in accord with all similar work on the new rays. The action of the molecule on the ray is an additive effect, but not the action of the ray on the molecule. If the action of the X-ray is assumed to be indirect, the extension of the general principle to the case of X-rays might be inferred from the knowledge that it holds for β rays.

2. The relative ionizations produced by equal absorptions of X-rays in the gases experimented upon are the same as those produced by the corpuscular radiations.

This is exactly what should happen if the ionization is all indirect. I have used the corresponding argument to prove the indirect character of the ionization by the γ rays (Phil. Mag. Sept. 1910, pp. 406-407).

3. When a mixture of two gases is traversed by the X-rays the observed ionization is the sum of the ionizations that would be observed if the same pencil of X-rays went through the gases separately.

Dr. Barkla considers that this result proves that much of the X-ray action is direct. Perhaps the point is best understood when the argument is put into mathematical form.

Let k_1 and k_2 be the mass absorption coefficients of the X-rays in two gases: in many of the examples given by Dr. Barkla the rays were Ag X-rays and the gases were ethyl bromide and air. Let λ_1 and λ_2 be the corresponding coefficients in the case of the cathode rays due to Ag X-rays. Let w_1 and w_2 be the masses of gas and air per c.c., and let the ionization in the gas be μ times the ionization in the air for the same expenditure of X or cathode ray energy.

The ionizations in gas and air would separately be proportional to $k_1 w_1 \mu$ and $k_2 w_2$: and Dr. Barkla finds that when gas and air are mixed the ionization is $k_1 w_1 \mu + k_2 w_2$, on the same scale.

But if the X-ray action is indirect, we should first suppose that the production of cathode rays is proportional to

$k_1w_1 + k_2w_2$, and that the ionization is given by

$$(k_1w_1 + k_2w_2) \frac{\lambda_1w_1\mu + \lambda_2w_2}{\lambda_1w_1 + \lambda_2w_2}.$$

This is not the same as $k_1w_1\mu + k_2w_2$, and in the case of Ag rays acting on mixtures of air and ethyl bromide the difference should be observable, on the assumption made by Dr. Barkla that $\lambda_1 = \lambda_2$. For instance, when k_1 is much greater than k_2 , as in this case: and when $w_1 = w_2$ the ratio of the two expressions is 0.85 nearly instead of unity: assuming $\mu = 1.4$.

I admit at once that, if work and assumptions are all correct, the difference should have been apparent. But two things may be pointed out. In the first place, Dr. Barkla's results would show that there is no indirect action, whereas it is well known that there is much of it. The fact is evident from the form of such curves as Beatty obtained (Proc. Roy. Soc. lxxxv, p. 230). If the ionization in the gas were all due to direct action it would be simply proportional to the pressure of the gas, and Beatty shows that this is far from being the case. Mr. Porter and I have made many similar experiments; in several of them Ag rays acted on ethyl bromide in a chamber lined with carbon or aluminium. Until the pressure of the gas is such that the cathode rays made in the gas can complete most of their paths within the ionization chamber, the increase of ionization with pressure is far less than it afterwards becomes. If Dr. Barkla's experiments do not reveal the existence of the large amount of indirect action which is known to exist, they cannot be held to prove anything definite as to the relative amounts of direct and indirect action.

The second point is that the whole of Dr. Barkla's argument turns on the supposition that $\lambda_1 = \lambda_2$ in all cases. This is Lenard's law; but it is not known for certain that it can be applied so generally. I think we must wait for further knowledge of the absorption—so-called—of cathode rays before we are influenced by arguments which assume the law of equal densities. I gather from the concluding sentences of Dr. Barkla's paper that he himself is impressed by this consideration.

Yours faithfully,
W. H. BRAGG.

Leeds, March 11.

LV. *On the Time Scale.* By E. BUCKINGHAM*.

IN the examination of our notion of time which is necessitated by recent speculations, one point hardly seems to receive the attention it merits. This is the evident fact that *in the nature of things* time is not a measurable quantity; that times can be numbered in accordance with any system we please which does not introduce ambiguity into the meanings of "before," "after," and "at the same time"; and that no system has any more justification than another, *a priori*.

We have a simple criterion by which we may decide whether two temperatures are the same or which is the higher. When we go farther and express temperatures or intervals of temperature by numbers, we do so by adopting an arbitrary convention for numbering temperature, in other words, a scale. With regard to time, the case is analogous. We can say that two events are simultaneous, or that one occurs later than the other, and all other observers will agree with us if they are situated as we are with relation to the two events. But when we go farther and say *how much* later one event is than the other, we adopt a scale for numbering time: we do not measure it in any proper sense, for a past interval of time cannot be superposed upon nor substituted for one now elapsing or to come, so that the fundamental operation which lies at the basis of all true measurement is not only absent but in the nature of things impossible. Tomorrow differs *qualitatively* from today, as the warmth of summer does from the chill of winter. As with temperature, our choice of a scale has been and always will be dictated solely by convenience and subject to arbitrary change whenever we change our minds as to what is most convenient.

Why is it that we use mean solar time instead of sundial time? Because if we use mean solar time a body not acted on by any push or pull that we can detect moves "*uniformiter in directum*." We can use Newton's first law if we adopt this mode of numbering time, but not if we adopt an essentially different one. Newton's laws are the simplest and most perspicuous summary of the facts of pure dynamics, and for this reason and this only, we adopt a time scale which shall make them a correct representation of the observed facts. In effect, we use the first law to fix our time scale. It would be an utter absurdity to say that we "assume" that time "really" does progress in this way. An assumption is a proposition of which the truth or falsity can be decided by reference to some independent criterion: a definition is neither true nor false, it is only useful or not

* Communicated by the Author.

useful. We *define* our time scale by saying that Newton's laws *shall* be true, simply because it pleases us to do so; and it pleases us because we prefer simple to complicated statements of fact, when our choice is free.

Now all this has reference to ordinary experience where the observers are all relatively at rest or nearly so. But if we drop this restriction, a different definition of the time scale may be more convenient; if so, we are entirely at liberty to adopt it, if we do not delude ourselves with any nonsense about clocks "running at a constant rate,"—the term "a constant rate" being quite meaningless except in connexion with some time scale outside of and independent of the clock itself.

The notion of time, as defined by reference to Newton's first law and to the measurable quantity length, is so ingrained in us that the symbol " t " in our equations seems to us as if it ought, somehow or other, always to stand for the old familiar mean solar time. In reality it stands for a derived quantity which may be defined by means of true, *i. e.*, measurable, quantities, through the mediation of Newton's laws or Maxwell's equations or any other statement of observed facts which we may happen to be interested in having appear in a particular form. In the past we have paid attention only to Newton's laws, defined the time scale by reference to them, and used the same time scale in all branches of physics. It now turns out that if the usual form of the electromagnetic equations is to be retained when velocities comparable with that of light are in question, the time scale must be defined by those equations, so that the facts of mechanics are no longer expressible by Newton's laws. And since such velocities occur practically only in connexion with electromagnetic experiments, it may quite legitimately be thought better to pay attention to the electromagnetic than to the mechanical equations when, as for these high velocities, a choice must be made.

Whether a quantity can be so defined that it may replace our familiar " t " in *all* the equations of physics, for observations made under all possible circumstances, and without requiring any too serious modifications in the forms of the equations, remains to be seen. If it can, we may find it well to adopt the new quantity and call it "time." But the task will not be accomplished by shutting one's eyes to the fact that any time scale is merely an arbitrary system of numbering successive events, nor by any use of clocks which run "uniformiter," when uniformiter is defined only by reference to the Latin dictionary.

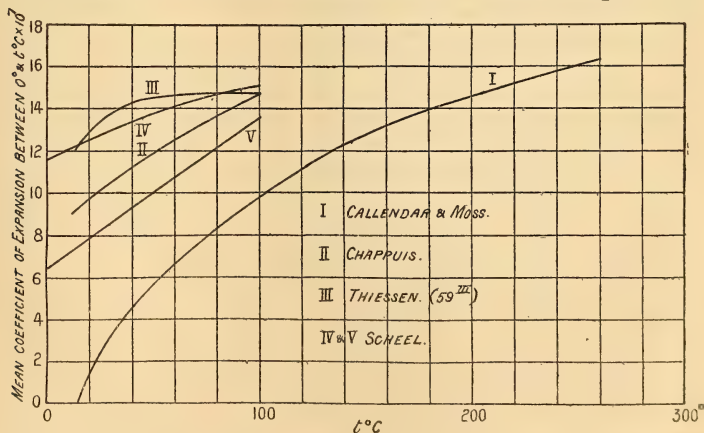
Washington,
February 15th, 1912.

LVI. *The Expansion of Mercury and of Quartz.*

By N. EUMORFOPOULOS, B.Sc. *

IN the March number of this magazine (p. 412) there is a paper by Scheel and Heuse on the expansion of mercury. In this paper two points are raised, first, the magnitude of the absolute expansion of mercury, secondly, whether it is permissible in work of the highest accuracy to calculate in the usual way the cubical expansion of a containing envelope from the linear value. Their views on this last point are not very definitely stated; it will perhaps be conducive to clearness if these two points are kept separate.

With regard to the first point, I am in perfect agreement with Scheel and Heuse that the value for the coefficient given by Callendar and Moss is too low, at all events below 100° , and that the mean value between 0° and 100° is approximately $\cdot 0001826$. In connexion with experiments in progress on the boiling-point of sulphur on the constant-pressure thermometer with a quartz bulb, I attempted, with the help of Mr. B. A. Keen, B.Sc., to determine the expansion of the bulb by a weight-thermometer method with compensated tubes †, using Callendar and Moss' coefficient for the expansion of mercury. The value at 100° was obtained in steam in the usual way; for the values at various temperatures up to 250° C. an oil-bath was used of the National Physical Laboratory pattern, for details of which I am indebted to Dr. J. A. Harker, F.R.S. These temperatures



were read with a platinum thermometer. From curve I. in the accompanying diagram it will be seen that Callendar

* Communicated by Prof. F. T. Trouton, F.R.S.

† See Proc. R. S. lxxxi. A (1908), p. 347.

and Moss' value for the expansion of mercury leads at low temperatures to inadmissible values for that of quartz. I have also plotted on the same diagram the expansion of the quartz, making use of Chappuis' value for mercury (curve II.), and also of Thiessen, Scheel, & Sell's value from the 59^{III} bulb (curve III.). For comparison curves IV. and V. are added; these are obtained from Scheel's values for the linear expansion of two different specimens of quartz, one of which indicated a maximum density at -46° C., and the other at -84° C. In interpreting the differences between the various curves, it should be remembered that an uncertainty of 1×10^{-7} in the coefficient of expansion of the bulb * leads to an uncertainty of .016 degree at the boiling-point of sulphur, and of approximately .1 degree at 1000° C. Without laying too much stress on the exact shape of the curve between 0° and 100° , it appears likely that the coefficient is still changing at 100° †, and, therefore, the same value cannot be used for the fundamental interval as for temperatures above 100° C. Hence it is insufficient to know with accuracy merely the fundamental interval of the weight thermometer. It may further be pointed out that judging from Scheel's two curves measurements on one specimen cannot, even for silica, be used with confidence for another.

With regard to the second point mentioned above, viz., the calculation of the cubical from the linear expansion, we must examine rapidly the various points of agreement mentioned in Scheel and Heuse's paper, to see how they affect the point we are considering.

The agreement mentioned in §2 (p. 413) between the expansion of mercury by the direct and indirect methods throws no light on this question: it merely indicates that Chappuis' measurements were carefully made, and that the two glasses behaved almost identically (they were both "verre dur"); the experiment is, in fact, merely the comparison (through the hydrogen thermometer) of the indications of a weight with an ordinary thermometer.

The next paragraph refers to the expansion of water. In comparing the weight-thermometer method with the absolute method, it will be better to take the values given by the latter as the standard ones, as we then get a fairer test of the proper allowance for the expansion of the bulb:

* The difference between Scheel's two values is at 100° about $1\frac{1}{2}$ times this quantity.

† Compare Randall, *Phys. Rev.* vol. xxx. (1910), p. 216.

Specific volume of water with respect to that at 4°.

Variations from the absolute value $\times 10^6$.

Temperature.	Chappuis. Verre Dur.	Chappuis. Platinum-Iridium.
0	-1	-1
10	-2	-3
20	-5	-3
30	-7	-4
40	-11	-5
100	-22	...

It will now be noticed that there is a systematic difference between the two sets of results. The platinum-iridium bulb (a more isotropic material) shows a better agreement. The glass bulb shows quite sensible differences. If then we can assume that the absolute method is free from systematic error, the only conclusion we can come to is that the expansion of the glass has not been properly allowed for. The linear expansion was, in this case, measured on the bulb itself, and hence should be especially reliable. It is noteworthy that Chappuis' value at 100° agrees well with that obtained by Thiessen, Scheel, and Sell with the weight thermometer, showing that, if the absolute method can be trusted, a similar error has been made in the two cases in allowing for the expansion of the glass.

The agreement in §5 (p. 415) is satisfactory as determining the fundamental interval for mercury. The values originally given varied from 18194 to 18257, when the expansion of the bulb was allowed for by the linear method. The agreement is thus obtained by frankly abandoning this method for the dilatation, and reverting to the absolute method. Chappuis' numbers, treated in the same way, lead to a somewhat higher value, viz., 18276; this should have been included in the list of §5, but it would have somewhat marred its symmetry.

The experimental evidence so far available thus seems distinctly against the calculation of the cubical from the linear expansion.

University College,
London.

LVII. *On the Law of Molecular Attraction.**To the Editors of the Philosophical Magazine.*

Cambridge, Feb. 21, 1912.

GENTLEMEN,—

IN a paper to the Philosophical Magazine of January Mr. Tyrer has investigated whether the function $\phi\left(\frac{T}{T_c}, \frac{z}{x_c}\right)$ in the law of molecular attraction does really contain the temperature T . The conclusions he arrives at are based on the statement in his paper, page 109, that “if the total change of energy of a liquid which expands at constant temperature is not entirely made up of the changes in the potential energies of attraction and of external pressure, then we should expect to find that the specific heat of a liquid at constant volume varies with the density.” But this statement is wrong.

Let us suppose that the attraction between two molecules depends on their temperature. The energy necessary to separate the molecules of a mass of substance from one another by an infinite distance against the molecular attraction may then be written $\psi(T, \rho)$, where ρ denotes the density of the substance. The expression for the specific heat at constant volume will then contain the term $\left\{ \frac{d(\psi(T, \rho))}{dT} \right\}_{\rho=\text{constant}}$. The specific heat is therefore not independent of ρ , and the above statement does not hold. One of the conclusions at which Mr. Tyrer arrives, namely that the attraction between two molecules is independent of their temperature, thus underlies his reasoning as an assumption.

It is very probable, however, that the change in potential energy of a substance with change of volume consists in part of a change in the internal energies of the molecules. But the latter quantity and the potential energy due to molecular attraction always occur together, and it is difficult therefore to disentangle them. However, I have obtained fairly conclusive evidence now that the attraction between two molecules depends on their temperature. A simple explanation of this property can be given.

Yours faithfully,

R. D. KLEEMAN.

LVIII. *A Relation between Coefficients of Expansion of Liquids and their Critical Temperatures.* By H. DAVIES, B.Sc., Head of Physics Department, Municipal College, Portsmouth*.

THE law of the "Rectilinear Diameter," as given by Mathias †, states that

$$D_l + D_v = a - bT, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where D_v and D_l are the densities of saturated vapour and liquid respectively, and T is the absolute temperature. As a deduction from this law Guldberg ‡ calculated the ratio of the densities at the critical temperature and at the absolute zero, finding a practically constant value 4 for it.

Let T_c , V_c , and D_c represent the critical temperature, the critical volume, and the density at the critical temperature.

For $T=0$, $D_v=0$, and $D_l=4D_c$. Hence in (1) $a=4D_c$.

For $T=T_c$, $D_l=D_v=D_c$, and $2D_c=4D_c-b \cdot T_c$,

$$b = \frac{2D_c}{T_c}.$$

Mathias' law can now be put in the form

$$D_l + D_v = 4D_c - \frac{2D_c}{T_c} \cdot T \quad . \quad . \quad . \quad (2)$$

At temperatures well removed from the critical temperature D_v is negligible in comparison with D_l . If V is the specific volume of the liquid, then

$$V = \frac{1}{D_l} = \frac{1}{4D_c - \frac{2D_c}{T_c} T} = \frac{T_c}{2D_c(2T_c - T)} \quad . \quad . \quad . \quad (3)$$

The coefficient of expansion $\alpha = \frac{1}{V} \cdot \frac{dV}{dT}$ and is obtained directly from (3), thus

$$\alpha = \frac{1}{V} \cdot \frac{dV}{dT} = \frac{1}{2T_c - T} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Equation (4) enables one to calculate the coefficient of expansion from the known critical temperatures, or conversely to calculate the critical temperatures from the experimental values of the coefficient of expansion.

* Communicated by Prof. A. W. Porter, F.R.S.

† *Journ. de Phys.* (3) vol. ii. 1893, p. 11; (3) vol. i. 1892, p. 53.

‡ *Chem. Cent. Bl.* 1898, vol. ii. p. 1042.

The right hand side of (4) can be expanded in a series with ascending powers of T giving the temperature variation of α . Thus

$$\alpha = \frac{1}{2T_c} + \frac{T}{(2T_c)^2} + \frac{T^2}{(2T_c)^3} + \dots \quad (5)$$

The experimental values of coefficients of expansion and of critical temperatures are commonly given with reference to the centigrade scale. To transform from absolute to centigrade scales it is better to start with equation (4). Thus

$$\begin{aligned} \alpha &= \frac{1}{2(\theta_c + 273) - (\theta + 273)} = \frac{1}{(2\theta_c + 273) - \theta} \\ &= \frac{1}{2\theta_c + 273} + \frac{\theta}{(2\theta_c + 273)^2} + \dots \quad (6) \end{aligned}$$

The values of the constant term are tabulated for some liquids below with the experimental values for comparison. They were selected quite at random from Landolt and Börnstein's tables.

TABLE I.

Liquid.	$\theta_c^\circ \text{C.}$	α (Calc.).	α (Exp.).
Acetone	237	·001339	·001324
Aniline	426	·000869	·00082
Bromine.....	302	·001167	·00104
Benzene	290	·001172	·001176
Pentane	197	·001499	·001464
Phenol	419	·00088	·000834
Toluol	321	·001062	·001028
Naphthalene	468	·00082	·00075
Thymol	425	·000889	·000843
Xylol-o	358	·00101	·00092
Xylol-m	346	·00103	·00096

The greatest difference between the experimental and calculated values occurs in the case of bromine, where it is nearly 12 per cent. The agreement in the other cases is very satisfactory.

The temperature variation of α can be calculated from the second and succeeding terms. The values of the coefficient of θ are given in Table II. with the corresponding values deduced from experimental data.

TABLE II.

Liquid.	Coef. of θ (Calc.).	Coef. of θ (Exp.).
Acetone	1.79×10^{-6}	5.83×10^{-6}
Aniline	$.79 \times 10^{-6}$	1.08×10^{-6}
Bromine	1.36×10^{-6}	1.71×10^{-6}
Benzene	1.375×10^{-6}	2.18×10^{-6}
Pentane	2.25×10^{-6}	4.08×10^{-6}
Phenol	$.78 \times 10^{-6}$	$.708 \times 10^{-6}$
Toluol	1.19×10^{-6}	2.49×10^{-6}
Naphthalene	$.67 \times 10^{-6}$	$.28 \times 10^{-6}$
Thymol	$.79 \times 10^{-6}$	$.43 \times 10^{-6}$
Xylol-o	1.02×10^{-6}	1.77×10^{-6}
Xylol-m	1.07×10^{-6}	1.02×10^{-6}

Not much weight can be attached to the values of the coefficients of θ as Mathias' law is not sufficiently accurate to allow of second-order quantities being deduced therefrom. The experimental values likewise are of doubtful value. It is interesting to note, however, that the order of magnitude agrees in every case.

The relation does not hold for liquids which show strong association. This was expected, as the law of the rectilinear diameter fails for such liquids.

Thorpe and Rücker* have obtained an equivalent result, and have shown how critical temperatures can be calculated from the formula

$$T_c = \frac{T_2 s_1 - T_1 s_2}{A(s_1 - s_2)},$$

where s_1 and s_2 are two densities of a liquid and A is a constant which they take to be 1.995. This can be changed into the form

$$\frac{s}{AT_c - T} = \text{constant},$$

which is equivalent to equation (4) above. They obtained their result by using an expression for the expansion of a perfect liquid†, proposed by Mendeleeff as a result of his experimental work on the Paraffins, coupled with Van der Waals' equation of state.

I wish in conclusion to thank Prof. A. W. Porter for his kindly help and criticism, and for supplying me with the reference to the work of Thorpe and Rücker.

* Thorpe & Rücker, Trans. Chem. Society, xlv. (1884).

† Mendeleeff, Trans. Chem. Soc. xlv. (1884).

LIX. *The Theory of Spectral Series.* By Prof. H. A. WILSON, F.R.S., F.R.S.C., McGill University, Montreal*.

AN important question with regard to the spectra of the elements is whether the different frequencies are due to the different modes of vibration of one kind of system or to the vibrations of systems of different kinds. In recent years the second alternative has come to appear the more probable.

Thus Ritz† in his earlier papers regarded the different lines as due to the different modes of vibration of a kind of two-dimensional system, but later he abandoned this theory and supposed the different lines due to different systems, each system having only one possible period.

Ritz obtained his different systems by supposing an electron to vibrate in the field on the axis of a bar-magnet which was built up of a varying number of elementary magnets. This theory, though undoubtedly useful and important, seems to the writer to be extremely artificial and improbable. Also it seems impossible to reconcile it with other theories of atomic structure such as Sir J. J. Thomson's well-known theory which, as far as can be seen at present, must contain a considerable element of truth.

On Sir J. J. Thomson's theory an atom consists of a sphere of positive electricity of uniform density containing negative electrons which can move about freely inside the sphere.

It is easy to show that such an atom has only one period of vibration which can produce appreciable radiation. For it is well known‡ that the radiation from a number of electrons occupying a volume of dimensions small compared with the wave-length of light is very approximately the same as that emitted by one electron moving with an acceleration equal to the resultant of the accelerations of all the electrons.

Take the centre of the positive sphere as origin and let

$$x, y, z, \quad x_2, y_2, z_2, \dots x_n, y_n, z_n$$

be the coordinates of the n electrons which it contains. The components of the resultant of the accelerations of all the electrons are

$$\ddot{x}_1 + \ddot{x}_2 + \dots = \Sigma \ddot{x}, \quad \Sigma \ddot{y} \text{ and } \Sigma \ddot{z}.$$

* Communicated by the Author.

† *Gesammelte Werke*, Paris, 1911.

‡ H. A. Lorentz, 'Theory of Electrons,' p. 120.

If $\bar{x}$, $\bar{y}$, $\bar{z}$ are the coordinates of the centre of mass of the n electrons we have

$$n\ddot{\bar{x}} = \Sigma \ddot{x}, \quad n\ddot{\bar{y}} = \Sigma \ddot{y}, \quad n\ddot{\bar{z}} = \Sigma \ddot{z}.$$

The radiation is therefore determined by the acceleration of the centre of mass of the electrons in the atom. This can be easily found, for each electron is attracted to the origin by a force $-\mu r$ proportional to its distance (r) from the origin and acted on by forces due to the other electrons. The forces between the electrons will not affect the motion of the centre of mass, so that we have

$$n\ddot{\bar{x}} = \Sigma \ddot{x} = -\frac{\mu}{M} \Sigma x = -\frac{n\mu}{M} \bar{x}$$

with similar equations for $\ddot{\bar{y}}$ and $\ddot{\bar{z}}$. Here M denotes the mass of one electron. Thus the centre of mass has three equal periods of vibration about the origin of period

$$T = 2\pi \sqrt{\frac{M}{\mu}}.$$

This therefore is the period of the radiation emitted by the atom, for all other possible periods are practically ineffective. We have also $\mu = \frac{4}{3}\pi e\rho$, where e is the charge on one electron and ρ the charge per c.c. in the positive sphere. Hence if $\nu = 1/\lambda$, where λ is the wave-length of the light emitted, we get

$$\nu = \sqrt{\frac{e\rho}{3\pi c^2 M}}$$

where c denotes the velocity of light.

It appears therefore that ν depends only on ρ since c , e , and M are constants. To explain the different values of ν in the spectra we must therefore suppose that ρ has different values in the molecules emitting the different lines.

There are two distinct ways in which ρ can be supposed to be changed. First we may suppose that when a number of atoms combine to form a molecule they produce a positive sphere of different density, so that if m denotes the number of atoms in a molecule we have a series of values of ρ corresponding to $m=1, 2, 3, 4 \dots$. Secondly, a molecule may lose a number of electrons, say n , and we may suppose that the loss of an electron produces a change in ρ .

According to this we should expect ρ and hence ν to be a function of the two integers m and n .

When two atoms combine there is as a rule a diminution

in the total volume. This has led Prof. Richards* to suggest that atoms are compressible and that when two combine the attraction between them produces a diminution of volume. Thus we should expect ρ to increase with m . Also as m gets larger we should expect the changes in ρ due to the addition of one more atom to become smaller, so that for very large values of m , ρ should obtain a limiting value.

As to n it is clear that an increase in the total charge on the atom must tend to increase its volume for the electric intensity at the surface tends to pull it outwards. We should therefore expect ν to diminish with n and to increase up to a limiting value with m .

The various series in the spectra of a particular element can be represented by formulæ giving ν as a function of two integers. Thus for hydrogen we have

$$\nu = N \left(\frac{1}{n^2} - \frac{1}{m^2} \right)$$

where N is a constant and n and m are integers.

For other elements we have according to Ritz

$$\nu = \frac{N}{(n+a+b/n^2)^2} - \frac{N}{(m+a'+b'/m^2)^2}.$$

If we give n a particular value we get a series of lines by changing m .

Recent investigations seem to show that these formulæ do not give the observed values exactly, so that it seems that they are after all only empirical and without very much physical significance. They do show, however, that ν is a function of two integers in many cases. Also we observe that increasing m in the above formulæ makes ν increase up to a limit, while increasing n diminishes ν .

We know too little of the nature of the positive electricity to be able to formulate a satisfactory theory of the variations in its density. The following is merely intended as an illustration to show that the theory proposed can lead to formulæ like Balmer's.

Let us suppose that the positive sphere behaves as though it had a surface-tension T , and that the relation between ρ and the pressure p due to T is $p = (\alpha\rho)^{\frac{1}{2}}$ where α is a constant. Suppose also that T is a function of ρ given by

$$T = \left(\frac{a}{b - \sqrt{\rho}} \right)^{\frac{1}{2}}$$

where a and b are constants.

* Faraday Lecture, 1911.

We have also $\rho = mE/V$ where $V = \frac{4}{3}\pi R^3$ is the volume of the sphere, R its radius, and E is the charge in the sphere of one atom.

Also $p = 2T/R$ and $\nu = \sqrt{ep/3\pi c^2 M}$.

Solving all these equations for ν we easily obtain

$$\nu = a' - b'/m^2,$$

where a' and b' are constants as in the hydrogen spectrum.

Some important facts receive a satisfactory explanation on the above theory. In flames, alkali metal salts only give one or two lines. This is because the salt vapour is very dilute and mixed with a relatively enormous amount of flame gases, so that it is extremely unlikely that more than one or two metal atoms should combine together. The greatest number of lines in the series is observed when the metal is heated in an exhausted tube. In this case the vapour is saturated and condensing in the cooler parts, so that the conditions are very favourable to the formation of molecules containing many atoms.

The flame lines appear to be emitted by uncharged molecules, so that for these lines we should have $n=0$. We can write $n+1$ or $n+2$ for n in the formulæ for ν in order to make them applicable when $n=0$.

The three hydrogen series are given by the formulæ

$$\nu = N \left(\frac{1}{4} - \frac{1}{m^2} \right) \quad m=3, 4, 5, \dots$$

$$\nu = N \left(\frac{1}{4} - \frac{1}{(m+0.5)^2} \right) \quad m=2, 3, 4, \dots$$

$$\nu = N \left(\frac{1}{9} - \frac{1}{m^2} \right) \quad m=4, 5, 6, \dots$$

The chief series may be supposed due to uncharged molecules containing an even number of atoms. The second series to uncharged molecules containing an odd number of atoms, and the third series to molecules each having lost one electron and containing an even number of atoms. All three series can then be represented by the formula

$$\nu = N \left(\frac{1}{(n+2)^2} - \left(\frac{2}{m+4} \right)^2 \right)$$

where n is the number of electrons lost by each molecule and m the number of atoms per molecule.

The first series due to the combination of ordinary molecules H_2 is naturally the one usually obtained.

LX. *The Effects of the Diurnal Rotation on the Upper Atmosphere.* By C. G. DARWIN, B.A.*

AS the earth rotates the forces of viscosity tend to drag the lower atmosphere with it, so that the mass motion of the air in this region has the same angular velocity as that of the solid earth itself. Now, at a certain height above the adiabatic region the density becomes so small that there are practically no collisions between the molecules, and here viscosity can therefore no longer have play. A molecule will rise from out of the collision region, perform a portion of an orbit, and then fall back again. Now, during its free path the angular momentum and not the velocity of the molecule is constant, and so it would be expected that at altitudes above the collision region the mean motion of the air would lag behind that of the earth. This paper was undertaken to find the amount of this lag. We shall see, however, that it is entirely counterbalanced by another effect. It is very probable that this may have been perceived by writers on the subject; but I have found no explicit statement of it; and the non-existence of the lag does not seem to me to be an obvious fact at first sight.

Suppose that there is a definite layer in the atmosphere, such that below it the gas is moving with the same angular velocity as the earth, and that above it there are no collisions. Let this layer be at a distance r_0 from the centre of the earth. Take spherical polar coordinates at the centre of the earth, fixed in direction. If we neglect for the present any molecules describing permanent orbits outside r_0 , all the gas at any greater height will be due to molecules projected from the sphere r_0 .

Consider a molecule projected from r_0, λ_0, l_0 with a velocity V_0 at angle θ_0 to the vertical in an azimuth ϕ_0 . Let this molecule pass through r, λ, l with velocity V in the direction θ, ϕ . The equation of energy then gives

$$V^2 - 2g \frac{a^2}{r} = V_0^2 - 2g \frac{a^2}{r_0},$$

g being the attractive part of gravity and a the earth's radius.

The equation of angular momentum gives

$$rV \sin \theta = r_0 V_0 \sin \theta_0,$$

and since the orbit is in a plane through the earth's centre, we have by spherical trigonometry

$$\sin \lambda_0 \sin \phi_0 = \sin \lambda \sin \phi.$$

* Communicated by the Author.

Let N_0 be the molecular density at the pole at height r_0 . If ω is the earth's angular velocity the density at a point of latitude λ_0 will then be $N_0 \exp. hmr_0^2 \omega^2 \sin^2 \lambda_0$ (h being inversely proportional to the absolute temperature of the isothermal region). Since the mass velocity of the air is $r_0 \omega \sin \lambda_0$ eastwards, the molecule we have considered above has, as components of molecular velocity,

$V_0 \sin \theta_0 \cos \phi_0$, $V_0 \sin \theta_0 \sin \phi_0 - r_0 \omega \sin \lambda_0$, $V_0 \cos \theta_0$,
southwards, eastwards, and upwards.

The number of molecules which have position and velocity in the element

$$r_0^2 \sin \lambda_0 dr_0 d\lambda_0 dl_0 \cdot V_0^2 \sin \theta_0 dV_0 d\theta_0 d\phi_0$$

is

$$N_0 \left(\frac{hm}{\pi} \right)^{\frac{3}{2}} \exp - hm(V_0^2 - 2V_0 \sin \theta_0 \sin \phi_0 r_0 \omega \sin \lambda_0) \\ \times r_0^2 \sin \lambda_0 dr_0 d\lambda_0 dl_0 V_0^2 \sin \theta_0 dV_0 d\theta_0 d\phi_0.$$

These molecules will all pass into the corresponding region at r, λ, l with the corresponding velocity V in direction θ, ϕ ; so that they will be in the element

$$r^2 \sin \lambda dr d\lambda dl V^2 \sin \theta dV d\theta d\phi.$$

Thus the number in this element is

$$N_0 \left(\frac{hm}{\pi} \right)^{\frac{3}{2}} \exp - hm(V_0^2 - 2V_0 r_0 \sin \theta_0 \cdot \sin \lambda_0 \sin \phi_0) \\ \times r^2 \sin \lambda dr d\lambda dl V^2 \sin \theta dV d\theta d\phi \\ = N_0 e^{-2hmg a^2 \left(\frac{1}{r_0} - \frac{1}{r} \right)} \left(\frac{hm}{\pi} \right)^{\frac{3}{2}} \exp - hm(V^2 - 2Vr \sin \theta \cdot \sin \lambda \sin \phi) \\ \times r^2 \sin \lambda dr d\lambda dl V^2 \sin \theta dV d\theta d\phi.$$

Put

$$N_0 e^{-2hmg a^2 \left(\frac{1}{r_0} - \frac{1}{r} \right)} = N,$$

the polar density proper to the height r on the ordinary kinetic theory. The distribution of velocities in unit volume at r then is

$$N \left(\frac{hm}{\pi} \right)^{\frac{3}{2}} \exp - hm(V^2 - 2V \sin \theta \sin \phi \cdot r \omega \sin \lambda) V^2 dV \sin \theta d\theta d\phi. \quad (A)$$

If we suppose this expression true for all values of V, θ, ϕ , it at once follows by integration that the density is $N e^{\frac{hmr^2 \omega^2 \sin^2 \lambda}{2}}$, the mass velocity is $r \omega \sin \lambda$ eastwards, and the temperature is $\frac{1}{2hR}$ (R being here the gas constant); and this is true for all regions above the adiabatic no matter what the height.

Thus collisions in the lower atmosphere are sufficient to reduce the upper regions to the state they would have if they were subject to collisions.

These facts may be deduced directly from the general kinetic theory of gases. For suppose that a smooth spherical envelope is placed at a considerable distance outside the earth. In this case, if sufficient time were allowed, the gas would ultimately attain accurately its normal distribution, while most of the molecules in the outer regions would be describing parts of orbits, having come from collision near perigee. The distribution of molecules will be given by (A), the assumption that all values of $V\theta\phi$ are possible being equivalent to the assumption of an envelope which returns molecules describing hyperbolic orbits, and the assumption of infinite time being equivalent to the assumption that the free orbits which never go inside r_0 are properly distributed.

Thus the lagging effect, which at first sight was expected, is entirely absent. This may be seen physically from the fact that the molecules projected eastwards from r_0 have, in general, greater velocities than those projected westwards, and so will tend to go higher. Thus, though every molecule has less velocity at r , the ratio of the number of molecules moving eastwards to those moving westwards is just so much greater than at r_0 that the mean angular velocity about the earth's axis is unaltered.

It has been stated that this result is subject to two corrections, one for hyperbolic orbits which cause permanent loss to the atmosphere, and the other for molecules describing free elliptic orbits which never cut r_0 . The first correction is known to be very small. Its general effect would be to impart an infinitesimal upward motion to the air. The second correction is subject to an essential uncertainty. For there must certainly be some molecules describing "external" orbits which do not cut r_0 . Originally each of these must have been caused by a collision outside r_0 , but as soon as we admit the existence of such collisions, the region at once becomes subject to the normal law of distribution. This correction is thus only needful at such heights that there have been very few collisions since the time when the angular velocity and temperature of the earth were markedly different. Considering how vague is our information of the state of the present atmosphere, it seems hopeless to estimate at all any effects remaining in it from the remote past. It is very doubtful also if such external orbits could persist for any long time. I am informed that up to a distance of about 10 earth's radii the orbits would be stable, but

meteorites must have been continually destroying them, so that it seems extremely doubtful if the history of the earth is now written in its atmosphere.

Even the sign of the correction is doubtful. For if external orbits are absent there will be a lag, whereas if there are any remaining from a period of faster rotation the motion will be greater than that of the earth. Under the circumstances the most that can be done is to estimate the effect when the orbits are supposed absent. For this purpose we must consider what values of V, θ, ϕ are to be excluded in obtaining the various averages. If particles are projected from r with all velocities in all directions, then since the orbits are reversible, those values of V, θ, ϕ are to be excluded which give rise to orbits never cutting r_0 . Take ρ, ψ as current coordinates in the plane of the orbit. Then

$$\dot{\rho}^2 + \rho^2 \dot{\psi}^2 = V^2 - 2ga^2 \left(\frac{1}{r} - \frac{1}{\rho} \right) \text{ and } \rho^2 \dot{\psi} = rV \sin \theta,$$

whence

$$\rho^2 \dot{\rho}^2 = -r^2 V^2 \sin^2 \theta + \rho^2 \left(V^2 - \frac{2ga^2}{r} \right) + 2ga^2 \rho.$$

The apses are given by making the right-hand side vanish.

For elliptic orbits $\frac{2ga^2}{r} > V^2$, and the apses are the roots of the equation

$$\left(\frac{2ga^2}{r} - V^2 \right) \rho^2 - 2ga^2 \rho + r^2 V^2 \sin^2 \theta = 0.$$

One of these roots is always greater than r . The condition for the second to be less than r_0 is

$$\left(\frac{2ga^2}{r} - V^2 \right) r_0^2 - 2ga^2 r_0 + r^2 V^2 \sin^2 \theta < 0.$$

If a molecule is returned for every molecule which goes to infinity with a hyperbolic orbit, the same condition will hold for these. If this is not assumed the solution would involve one root of this quadratic and would be rather complicated. The equation may best be understood geometrically. Let uvw , the three components of velocity, be represented as cartesian axes. Then the distribution of velocities is

$$N \left(\frac{hm}{\pi} \right)^{\frac{3}{2}} e^{-hm(u^2 + v^2 + w^2 - 2vrw \sin \lambda)} du dv dw$$

for values of uvw inside the hyperboloid

$$\frac{2ga^2}{r} - (u^2 + v^2 + w^2) - \frac{2ga^2}{r_0} + \frac{r^2}{r_0^2} (u^2 + v^2) = 0.$$

The density, velocity, and temperature may be approximately evaluated by the use of spheroidal coordinates, but the process is rather laborious and I shall merely state the nature of the result. This depends on the position of the point under examination with regard to a certain surface defined by the equation

$$r^4 + r_0 r^3 = \frac{2ga^2}{\omega^2} r_0 \operatorname{cosec}^2 \lambda.$$

This surface is somewhat similar to the surface of minimum pressure and lies a little inside it. If $r_0 = 2a$, which is roughly the value it should have, then the surface cuts the equator at $5.4a$. The approximation goes as follows:—For points well inside the surface the correction is very small. Taking an atmosphere of hydrogen at 30° abs. it is about 1 mm. per sec. at $r = 4a$ at the equator. On approaching the surface the lag increases rapidly, while the density diminishes little apart from the ordinary diminution due to height. Outside the surface the density falls off very quickly and the lag changes slowly. In this region there is certainly a large disturbing factor in the presence of molecules describing hyperbolic paths and also in reality there must be many molecules describing permanent elliptic orbits.

It is therefore possible to say that no lagging effect will appear up to somewhat more than four radii from the earth's centre. Any discussion of phenomena at a greater height would have to take the hyperbolic paths into account and the presence of permanent orbits and probably also the arrival of molecules from outer space. These last two factors are entirely unknown and the density is very small, so that a fuller investigation does not seem advisable.

My thanks are due to Dr. Schuster for suggesting to me this problem, and for the interest he has taken in it.

The University,
Manchester.

LXI. *Note on the Electrical Resistance of Xylol-Alcohol Mixtures.* By NORMAN CAMPBELL, Sc.D.*

IN the Philosophical Magazine for August 1911, pp. 301, 302, I described certain liquid resistances which may be used for the same purposes as the resistances of ionized air generally associated with the name of Bronson. Some further investigation has been made into such properties of the liquids as are important for these purposes.

* Communicated by the Author.

The resistances may be made with commercial xylol and absolute alcohol which has been distilled from lime. The xylol possesses no appreciable conductivity, and no useful purpose is served by drying the alcohol further. The conductivity of the mixture, when the proportion of alcohol does not exceed some 12 per cent., increases much more rapidly than the concentration of the alcohol. When the proportion of alcohol exceeds some 12 per cent., the mixture ceases to obey Ohm's law accurately. The most convenient mixture to use contains 1 part of alcohol to 10 parts of xylol. The specific resistance of this mixture is of the order 10^{10} ohm. A resistance suitable for electrostatic measurements should generally not exceed 10^{12} ohms; a resistance of that magnitude can be made conveniently from a piece of quill tubing about 15 cm. long bent into a U-form. Electrodes can be made of copper or zinc as well as of platinum. Of course the liquid must be hermetically sealed in glass, if the resistance is to be constant.

Unfortunately the resistance of the mixture has a large temperature coefficient. Between 15° and 30° the resistance at a temperature t is given by

$$R_t = R_{20} \{1 + 0.014(t - 20)\}.$$

A temperature lower than 15° should not be used; it was found impossible to obtain consistent readings below that temperature.

The liquid resistances appear to me to have every advantage over "Bronson" resistances, except in the matter of sensitiveness to change of temperature. In most experiments ample accuracy can be attained by correcting for the temperature, while if extreme accuracy is required it is easy to maintain a constant temperature in a thermostat. The resistance can be determined readily in absolute measure by comparison with a wire megohm. For this purpose a series of resistances ranging from 3×10^7 ohm to 10^{12} ohm were made, each resistance being about 15 times greater than the next lower. The comparison is easily effected by a Wheatstone bridge in which a sensitive electrometer (3000 divisions for a volt) is substituted for the ordinary galvanometer. The points of the bridge which are usually connected to the galvanometer are connected one to earth and the other to one pair of quadrants of the electrometer, of which the other pair of quadrants is earthed; the other arms of the bridge are taken from a Post Office Box. The resistance between the battery and earth must be large compared to that in the Post Office Box.

It is probable that a detailed investigation into the relation between the conductivities of these mixtures and their composition would throw valuable light upon the mechanism of the conduction. The interesting fact is to be noted that the resistance, like that of metals and unlike that of electrolytes, increases with the temperature. The problem is recommended to the attention of those who are seeking matters for research. It is possible also that other liquid mixtures would be found more suitable than that of xylol and alcohol.

Leeds, Feb. 1, 1912.

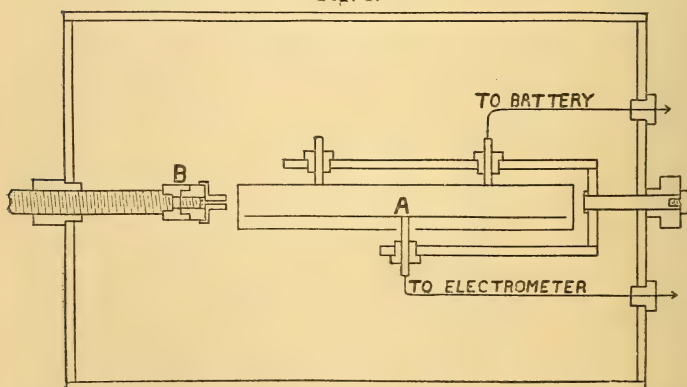
LXII. *A Determination of the Number of Ions produced by an Alpha Particle from Polonium.* By T. S. TAYLOR, Ph.D.*

Introduction.

THE investigations herein described were undertaken for the purpose of making a direct determination of the number of ions produced by an alpha particle from polonium. This consisted in measuring the saturation-current produced in an ionization vessel by a limited beam of rays from polonium, the determination of the capacity of the measuring system, and the counting of the number of alpha particles producing the ionization current by means of the scintillations they produce on a zinc sulphide screen during a given interval of time.

Description of Apparatus.

Fig. 1.



The essential parts of the apparatus, used in the determination of the saturation current, are shown in figure 1. The

* Communicated by the Author.

brass plate "A," about 8 centimetres long by 8 millimetres wide, was insulated by an amber plug as shown, and connected to one pair of the quadrants of a sensitive Dolezalek electrometer. The plate "A" was surrounded by a brass box about 8.3 centimetres long, 12 millimetres wide, and 12 millimetres deep. This box had a small opening, as shown at the left side, for allowing the alpha particles to enter it. This box together with the plate "A" comprised the ionization-chamber, since "A" was connected to the electrometer and the box surrounding it was joined to a high-potential battery of 750 volts. This voltage was sufficiently high to produce saturation current under normal atmospheric pressure. The source of rays was a preparation of polonium mounted within the brass plug "B," upon the end of a screw of one millimetre pitch. The brass plug was insulated from the screw by means of an amber washer under it. By means of the screw, the polonium could be moved toward or away from the left end of the box forming the outer wall of the ionization-chamber, and its position determined at any time. A brass cap, having a small hole of $\frac{1}{2}$ millimetre diameter and 8 millimetres long in it, was fitted over the brass plug "B" containing the polonium. This cap served to limit the beam of emergent rays such that they would not strike the walls of the ionization-chamber before they had reached the end of their path. The ionization-chamber, &c. were enclosed in a metal case, as shown in figure 1. The metal case was always connected to earth.

Determination of Capacity.

The capacity of the measuring system was determined by the method outlined by Campbell* for measuring small electrostatic capacities. A special auxiliary air-condenser was constructed to be used in the determination of the capacity of the measuring system. This capacity consisted of a brass plate 10 centimetres long by 7 centimetres wide within a brass box 12 centimetres long, 8 centimetres wide, and 1 centimetre high. The brass plate was insulated from the box by means of an amber plug through which a small rod supporting the plate was inserted. The entire box was enclosed in a metal case connected to earth. The box was insulated from the case, however, by means of hard rubber supports. The inner plate was always connected to the inner coating of the measuring system during the determination of the capacity.

* Campbell, Phil. Mag. vol. xxi. pp. 42-45, January 1911.

The standard condenser used was a Leeds and Northrup microfarad condenser having elements 0.5, 0.2, 0.2, 0.05, and 0.05 microfarad. The calibration of this condenser shows the above values to agree with Leeds and Northrup's standard capacity within one fourth of a per cent. By connecting the elements of this condenser in series, capacities of 0.025 and 0.02 microfarad were obtained. In this determination care was taken to shield the connecting wires joining the auxiliary condenser and the standard condenser to the measuring system from outside electrostatic influences. This was done by enclosing all connecting wires in earthed metal conductors. Mercury contact-keys were used in making the connexions between the auxiliary condenser, the standard condenser, and the measuring system, so that either condenser could be joined in parallel with the measuring system as desired.

A potentiometer scheme was used for charging the outer coating of the auxiliary condenser. This consisted of several 100,000 ohm resistance-coils and coils ranging from 1 to 100,000 ohms, in series with a 500 volt storage-battery. By this means, any fractional part of the 500 volts could be applied to the outer coating of the auxiliary condenser. Using values of the standard condenser equal to 0.025 and 0.02 microfarad, respectively, the values of the capacity of the measuring system as recorded in Table I. were found.

TABLE I.

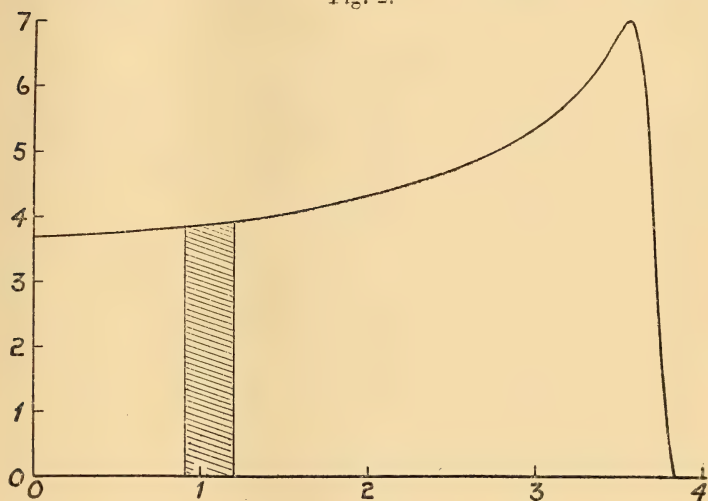
Value of standard capacity used, in microfarads.	Calculated capacity of the measuring system, in electrostatic units.
0.025	55.3
0.025	54.8
0.020	54.9
0.020	55.4
0.020	54.8
Mean 55.0	

The greatest variation from the mean value is seen to be less than one-half per cent., which is as small a variation as one might expect to obtain in the determination of so small an electrostatic capacity.

Measurement of Ionization Current.

The brass plug containing the polonium, with the cap over it for limiting the emergent beam of rays, was placed in an apparatus similar to that used in previous experiments *, and the Bragg ionization curve determined. Such a curve, thus obtained, is shown in figure 2. The plug with the cap over it was then placed in the apparatus (fig. 1) in position "B," and the screw, upon which it was fixed, turned so that the polonium was as close to the ionization-chamber as possible. This distance was 9 millimetres. The pressure of the gas in the air-tight vessel surrounding the ionization-chamber was then adjusted so as to be exactly 76 centimetres of mercury.

Fig. 2.



The ordinates are the deflexions in scale-divisions of the electrometer-needle per second. The abscissæ are the distances in centimetres of the polonium from the ionization-chamber.

This adjustment gave the alpha particles the same range in the different determinations. With a potential of 750 volts on the outer coating of the ionization-chamber, observations were made of the deflexion of the electrometer for intervals of 5 minutes. This deflexion of the electrometer-needle gave a measure of the ionization current that was produced by $(3.86 - 0.90)$ 2.96 centimetres of the range of the alpha particle. That is, it was proportional to the ionization that is represented by the area under the ionization curve in fig. 2 to the right of the ordinate corresponding to the abscissa 0.9 centimetre.

* Taylor, *Phil. Mag.* vol. xviii. p. 604, October 1909.

The polonium was then moved so as to be 1.2 centimetres from the ionization-chamber, and readings were taken of the deflexions of the electrometer for intervals of 5 minutes. The value of this deflexion gave a measure of the ionization current produced by 2.66 centimetres of the range of the alpha particle. This was proportional to the ionization that is represented by the area under the ionization curve to the right of the ordinate corresponding to the abscissa 1.2 in fig. 2.

The difference between the readings obtained when the polonium was 0.9 centimetre and 1.2 centimetres from the ionization-chamber gave a value that is proportional to the ionization represented by the area of the shaded portion of fig. 1. By comparing the area of this shaded portion with the area under the curve to the left of the abscissa 0.9, the amount that should be added to the electrometer reading in order to take account of the ionization produced in the first 0.9 centimetre of the path was obtained. This value could also be obtained by comparing the area to the left of the ordinate corresponding to the abscissa 0.9 in fig. 2 with the area to the right of the same ordinate.

The corrected reading of the electrometer, that is, the reading obtained when the polonium was 2.96 centimetres from the ionization-chamber plus the value corresponding to the first 0.9 centimetre of the path obtained in the above manner, gave a measure of the potential that the plate "A" and the electrometer system would have assumed had the beam of particles spent their entire range in the ionization-chamber. The corrected scale-readings, that would correspond to the ionization that would be produced by the entire range of the beam of rays used, are given in column 1, Table II. Each of the values given is the mean value of several separate determinations. By multiplying this corrected electrometer deflexion by the value of a scale-division in electrostatic units, the potential to which the plate "A" had been raised was obtained. One centimetre scale-deflexion corresponded to a potential of 4.39×10^{-5} electrostatic unit. The potentials in electrostatic units corresponding to the above cited corrected scale-deflexions are recorded in column 2, Table II. From the values of the potential and the capacity of the system, the quantity of electricity that would be given to the plate "A" by the total beam used was calculated. These values of the charge given to the plate "A" during the time of an observation (5 minutes) are recorded in column 3, Table II.

Determination of Alpha Particles in Beam.

The plug containing the polonium, with the cap for limiting the beam of rays over it, was removed from the apparatus and the number of alpha particles emerging in the beam determined by counting the number of scintillations produced per minute upon a zinc sulphide screen. A zinc sulphide screen purchased of Harrison Glew of London, and a microscope, composed of a Leitz objective number "4" and a Leitz eyepiece number "0," were used in the counting of the scintillations. The screen was standardized by using a small quantity of the active deposit of radium emanation for which the alpha ray activity was calculated from the

TABLE II.

Corrected deflexion corresponding to total ionization.	Potentials in E.S.U. corresponding to deflexions in column 1.	Charge that would be given to plate "A" by entire beam used,	Number of particles entering chamber in 5 minutes.	Ions produced by single alpha particle.
17.20	7.55×10^{-4}	4.15×10^{-2}	547	163,000
16.96	7.45×10^{-4}	4.09×10^{-2}	536	164,000
16.62	7.30×10^{-4}	4.01×10^{-2}	520	165,000
16.16	7.10×10^{-4}	3.90×10^{-2}	509	165,000
15.80	6.94×10^{-4}	3.82×10^{-2}	503	163,000
Mean value of ions produced.....				164,000

gamma ray activity. By this process it was found that 86 per cent. of the alpha particles striking the screen produced scintillations that were readily counted. A large number of determinations of the number of scintillations produced was made for each separate determination of the ionization current. The mean value of each series of these determinations was then corrected to take account of the fact that only 86 per cent. of the alpha particles striking the screen produced scintillations. These values were then multiplied by 5 in order to get the total number of alpha particles that entered the ionization-chamber during the time required to make one observation of the ionization current. This mean value of the number of alpha particles entering the ionization-chamber is recorded in column 4, Table II., for each determination.

Calculation of the Number of Ions and the Energy required to produce an Ion.

To get the number of ions produced by an alpha particle, the values of the charge given to the plate "A," as recorded in column 3, were divided by the corresponding values of the number of alpha particles that entered the chamber, as recorded in column 4, and the result divided by the value of the charge of an ion, which in this case was taken as 4.67×10^{-10} electrostatic unit. The values of the number of ions produced by an alpha particle, as determined in the above manner, are recorded in column 5, Table II. The mean of the different values found is seen to be 164,000.

It has been shown* that the rate of production of ions by an alpha particle is proportional to the rate of consumption of its energy. Hence it is possible to calculate the relative amount of energy that is required to produce an ion in air. Taking the value of e/m for the alpha particle as 5×10^3 electromagnetic units, the initial velocity as 1.68×10^9 cm./sec., and the charge e as 3.1×10^{-20} electromagnetic unit, the kinetic energy of the alpha particle is equal to

$$1/2 mv^2 = 1/2 m/ev^2 e = 8.7 \times 10^{-6} \text{ erg.}$$

Dividing this value by the number of ions produced (164,000) the relative amount of energy required to produce an ion is obtained. This gives a value of 5.3×10^{-11} erg.

Conclusions.

The number of ions produced by an alpha particle from polonium has been determined by a direct process and the mean value found to be 164,000. This value is in close agreement with that already found by Geiger†.

The relative amount of energy of an alpha particle required to produce an ion is calculated to be 5.3×10^{-11} erg.

Physics Building, University of Illinois,
Urbana, Illinois.

* Geiger, Proc. Royal Society, Series A, vol. lxxxiii. No. 565, p. 505; Taylor, Phil. Mag. April 1911.

† Geiger, Proc. Royal Society, Series A, vol. lxxxii. pp. 486-495, July 31, 1911.

LXIII. *The Charges on Ions.**To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

IN a paper by Mr. J. C. Pomeroy, published in the January number of the *Philosophical Magazine*, some experiments are described from which the author draws a number of conclusions as to the values of the charges on ions produced by a hot wire in air and in hydrogen at atmospheric pressure.

The experiments are said to have been made on the same principle as that which I used some time ago for finding the product $N.e$ for ions in different gases, N being the number of molecules per cubic centimetre of a gas at normal pressure and temperature, and e the charge on an ion. There is one fundamental condition on which the success of this method depends, which is that the experiments must be conducted at low pressures, except in the rare cases when such small densities of ionization are used that the electrical measurements can only be made by a sensitive electrometer when the charges on the electrodes have been accumulating for some hours.

Mr. Pomeroy has made his experiments at high pressures with densities of ionization which obviously are not very small, and the consequence is they furnish no evidence in support of the conclusions he has adopted.

It may perhaps prevent the recurrence of a similar error if I point out why it is necessary to work at low pressures in order to determine the value of $N.e$ by experiments on the lateral diffusion of a narrow stream of ions moving under an electric force. The principle of the method consists in producing ions on one side of a disk A, the disk being a thin sheet of metal with a circular aperture in the centre through which the ions can pass. On the other side of the disk the ions travel through a field of uniform electric force X , and are received by a circular disk B and a broad ring C surrounding the disk, a narrow air-gap being left between them for purposes of insulation. The disk B is directly opposite the aperture in the plate A and is of the same area as the aperture. All the ions are not received on the disk as the stream opens out and part of the charge is received by the ring C. There are two causes which contribute to the opening out of the stream—the diffusion of the ions, and their self-repulsion.

The effect of diffusion is, in these cases, independent of

the pressure, and if that process alone were acting, the ratio of the charge acquired by the disk to the total charge coming through the aperture would depend only on the product $N.e.X$. In the particular form of apparatus which I used and which was also used by Mr. Pomeroy, the disk should receive one half the number of ions coming through the aperture when $X=1.4$ volts per centimetre and $N.e$ has the normal value 1.23×10^{10} . As the plate A was at a distance of 7 centimetres from the electrodes B and C, the potential difference between the plate and the electrodes is in this case about 10 volts. A smaller voltage would be necessary if the disk receives a smaller proportion of the charge.

The effect of self-repulsion acts according to different laws, it increases with the pressure of the gas and also with the density of ionization. It is easy to see that if ρ is the charge per cubic centimetre of a distribution of ions at a point moving with the ions, the density ρ diminishes with the time t according to the formula

$$\frac{\rho}{\rho_0} = \frac{1}{1 + 4\pi k \rho_0 t},$$

ρ_0 being the initial value of ρ and k the velocity of the ions under unit electrostatic force. An approximate estimate of the effect of self-repulsion in expanding the section of the stream may be obtained from this formula. Let Q_0 be the charge coming through the aperture per second, s the area of the aperture, the charge ρ_0 per cubic centimetre of the gas is $\rho_0 = Q_0/s.k.E$, E being the force in electrostatic units in the space between the plate A and the electrodes. The ratio of the charge received by the disk to the charge coming through the aperture is ρ/ρ_0 , and in the time t the ions travel 7 centimetres under the force X so that $t = 7/kE$. Hence

$$4\pi k \rho_0 t = 4\pi k \cdot \frac{Q_0}{s.k.E} \cdot \frac{7}{kE} = \frac{28\pi Q_0}{s.k.E^2}.$$

This quantity must be small as compared with unity in order that the effect of diffusion may be the predominating factor in expanding the stream when the value of E is of the order $1.4/300$. To secure this condition at atmospheric pressure where k is the velocity due to unit force, it would be necessary to reduce Q_0 to such a small value that it would be very difficult to detect the charges acquired by the electrodes unless the observations extended over some hours. At a pressure of 10 millimetres, 76 times as great a charge can

be used, since k is inversely proportional to the pressure, and accurate measurements of the value of $N \cdot e$ may be deduced from observations that require a few minutes to collect the charges on the electrodes.

Mr. Pomeroy does not give the values of the charges acquired by the electrodes in his experiments, and his reasons for neglecting the effect of self-repulsion are unsatisfactory. In some of the experiments the potential of the plate A was raised to 200 volts, and it was concluded that the charge on each ion was equal to one atomic charge. And in others the potential was 100 volts and the charge was in these cases said to be two atomic charges. Apparently the ring and the disk acquired equal charges, in these experiments.

The theory of the experiments, however, shows that, when the ions have single atomic charges, and the opening of the stream is due to diffusion only, the ring B and disk C acquire equal charges when the potential of A is 10 volts. If Mr. Pomeroy is correct in supposing that the self-repulsion may be neglected, the logical conclusion to which his experiments lead is that in some cases the charges on the ions with which he was dealing were one-tenth, and in other cases one-twentieth of the atomic charge on a monovalent atom in a liquid electrolyte.

Yours truly,

JOHN S. TOWNSEND.

LXIV. *On the Absolute Expansion of Mercury. Reply to Criticisms by Scheel and Heuse. By H. L. CALLENDAR*.*

IN the March number of this Journal Scheel and Heuse have pointed out that our recent results for the absolute expansion of mercury do not agree quite so closely with previous determinations by indirect methods as the latter agree among themselves, and have drawn the conclusion that the discrepancy must be due to an error in our measurements. They also complain that we have neglected to bring into the discussion the experiments made at the Reichsanstalt in 1895 on the expansion of mercury by the weight thermometer method, and that we have omitted to discuss the results in relation to the expansion of water. This omission was not due to any oversight on our part, but to a natural desire to avoid the appearance of going out of our way to criticise the results of old experiments to which the Authors themselves did not seem at the time to attach much importance as a

* Communicated by the Author.

determination of the absolute expansion of mercury. The remarks of Messrs. Scheel and Heuse compel us, in self defence, to criticise these observations, and supply certain details which they have omitted. In order to confine our reply to a reasonable length, and to avoid thermometric difficulties, our remarks will be limited to the expansion from 0° to 100° C. All differences will be expressed in terms of the unit adopted by Messrs. Scheel and Heuse, namely, one part in a million of the volume at 0° C.

Mercury Weight Thermometer Method.—This method was applied by Thiesen, Scheel, and Sell between 0° and 100° C. to five bulbs, two of Jena glass 16^{III} , two of Verre Dur, and one of Jena glass 59^{III} . The cubical expansion of the bulbs was deduced from observations of the linear expansion of rods of the same glasses. The final results for the expansion of mercury, as deduced from these bulbs, are printed in heavy type near the end of their paper, and were as follows:—

From dilatometer 16^{III}	No. 1	·0182327
" "	No. 2	·0182091
" Verre Dur	No. 1	·0181934
" "	No. 3	·0181944
" "	59^{III}	·0182570

The differences in the results, covering a range of 63 units (neglecting the seventh decimal place as uncertain), greatly exceed the possible errors of observation in so simple an experiment, and may have arisen from three different causes: (1) The bulbs and rods, though specially selected for the experiment, may have differed in composition. (2) They may have differed in expansion owing to difference of form and treatment. (3) Even if the axial expansion of the bulbs were the same as that of the rods, the radial expansion, which is twice as important, might have been appreciably different. The results from the 16^{III} bulbs were discredited because they differed by 23 units, whereas the *verre dur* bulbs were in practical agreement, though much lower than either of the others. There was nothing, however, to show that the 59^{III} glass would have given more concordant results than the 16^{III} , if more than one bulb had been tested. It is hardly fair now to lay special stress on the highest result in place of the mean ·018245 of the two highest results adopted in the original paper.

The result of Chappuis obtained with a *verre dur* bulb is clearly entitled to much greater weight because it escapes the first two objections above given, since the linear expansion

of the bulb itself was measured. It is still, however, liable to the third objection. In fact a difference of little more than 2 per cent. between the radial and axial expansions of the bulb would suffice to bring his results into agreement with ours for the absolute expansion.

Expansion of Water.—By testing four of the same bulbs filled with water, Messrs. Thiesen, Scheel, and Sell obtained a comparison between the expansion of water and mercury in which the expansion of the glass was eliminated. Assuming the expansion of mercury between 0° and 100° C. to be $\cdot 018245$, they deduced the expansion of water between the same limits. But the converse method does not appear to be satisfactory for deducing the expansion of mercury, because the errors of observation or manipulation (arising chiefly from the water results at 100° C.) covered a range of no less than 28 units. Even the mean results for each bulb quoted by Scheel and Heuse can hardly be said to agree satisfactorily for this purpose, since they differ by 13 units, which would be an excessive error for a mercury weight thermometer, apart from the uncertainty of the expansion of the bulb.

The absolute determinations of the expansion of water by Thiesen over the range 0° to 100° C. were made with a single pair of columns 2 metres high and nearly 2 metres apart. The temperatures of the columns were taken at two points with mercury thermometers. The variation of the results at 100° C. covered a range of 64 units, corresponding to a variation of only 0.13 mm. in the manometer. In our mercury apparatus six pairs of columns were employed, giving an effective height of 11.6 metres, and the variation of the results for the fundamental interval covered a range of only 5 units, corresponding to 0.06 mm. Thiesen's mean results for water exceeded those found by Chappuis with the *verre dur* bulb by 22 units at 100° C., and by 11 units at 40° C. Considering the extreme difficulty of the determination of the absolute expansion of water, and the additional uncertainty of the weight thermometer comparisons, it does not appear that so much weight should be attached to this indirect method of deducing the expansion of mercury, as the ingenious mode of presentation adopted by Messrs. Scheel and Heuse might seem at first sight to indicate.

Expansion of Silica.—We have ourselves supplied the only serious objection adduced by Messrs. Scheel and Heuse which rests on the close agreement of Harlow's silica bulbs with the *verre dur* bulb of Chappuis for the fundamental interval, when the cubical coefficient of expansion is assumed to be

three times the linear in each case. I became aware of this coincidence some two years ago when the first results with the silica weight thermometer were obtained in my private laboratory, but we were unable to detect any source of error in our experiments sufficient to account for the discrepancy, and we were not in a position to discuss it at the time when our paper was published. I am at present inclined to the opinion that the explanation must be sought in the inequality of axial and radial expansion of a drawn tube due to intrinsic strain. It is difficult to see how this effect, if it exists, could be satisfactorily detected except by reference to the absolute expansion of mercury. The intrinsic strain in a hard glass tube appears to be of the same order as in a silica tube when tested by polarized light, and would probably produce the same absolute effect on the expansion. On this view it is necessary to suppose that the anomaly giving rise to a minimum length for a silica rod between -50° and -80° C. affects the radial expansion at a somewhat higher temperature, giving a minimum in the neighbourhood of 0° C. It is at least noteworthy that, if our results for the absolute expansion of mercury at 184° C. are assumed, the cubical coefficient of silica is already nearly three times the linear, when the latter has nearly reached the constant value which, according to my experiments*, it retains over the range 300° C. to 1400° C. But for the anomaly in the expansion of silica at low temperatures, and the impossibility of annealing it satisfactorily owing to its rapid devitrification at temperatures above 900° C., a silica bulb, employed according to Chappuis's method, would afford an almost ideal method of determining the expansion of a liquid. The measurement of the absolute expansion of mercury by the hydrostatic method is a difficult experiment, and may possibly involve sources of error which are not taken into account in the accepted theory. These are being further investigated, and the observations with the silica weight thermometer are being extended to higher and lower temperatures. It may be objected that such investigations should not be undertaken by amateurs in their occasional intervals of leisure, but should be confined to National Physical Laboratories, where the experimentalist may devote his whole time and attention to one research. In our case it may be urged in extenuation that the method was designed, and the chief part of the apparatus constructed, before the National Physical Laboratory existed. The work has been carried through under considerable difficulty, and is doubtless not so perfect as it should be. The apparatus was designed for working up to 300° C., and is perhaps not

* Shenstone, Proc. Roy. Inst. 1901. Not quoted by Scheel & Heuse.

so well suited for attaining the greatest precision at ordinary temperatures. The results at high temperatures are confirmed by the expansion of silica, and may probably be accepted with confidence. The apparent discrepancy at low temperatures is receiving further attention, but may be due simply to anomalies in the expansion of solids which are here most in evidence. We make no claim to infallibility, and do not expect anyone to adopt our "comprehensive tables" to the exclusion of others which they may consider more reliable. We ask only that our work may be regarded as an honest attempt to solve a difficult experimental problem, and we take this opportunity of thanking our fellow-workers, especially M. Pierre Chappuis, for the generous appreciation which they have so freely expressed of our labours.

LXV. *On the Absorption of Röntgen Rays in Air.* By A. S. EVE, D.Sc., and F. H. DAY, M.Sc., McGill University, Montreal*.

THE coefficient of absorption of the Röntgen rays in air was first determined by Rutherford† for a very soft bulb, and the value found was $\lambda = 0.001$. A thorough investigation of the absorption of the very penetrating radiations from a hard bulb was subsequently made by Rutherford and McClung‡, who found $\lambda = 0.000279$. Two pencils of rays passed down two long cylinders to suitable testing-vessels connected to an electrometer. The pressure in one cylinder was maintained constant, and in the other cylinder it was varied, and in this way the coefficient of absorption by air and by various gases could readily be determined.

It has been pointed out by one of us§ that, with any ionizing point-source, the coefficient of absorption in the atmosphere near the earth's surface can easily be obtained by varying the distance between the source of the rays and a testing electroscope. If I is the ionization current in the electroscope at a distance r from the source of the rays, I varies as $e^{-\lambda r}/r^2$. If distances r_1, r_2 give ionization currents I_1, I_2 , it follows that λ may be found from

$$\log_e I_1 r_1^2 - \log_e I_2 r_2^2 = \lambda(r_2 - r_1).$$

Preferably a number of distances and ionization currents are measured, and the line

$$\log_e I r^2 = A - \lambda r$$

is plotted with r as abscissa and $\log_e I r^2$ as ordinate. The

* Communicated by the Authors.

† Phil. Mag. Jan. 1899.

‡ Phil. Trans. Roy. Soc. (A) cxcvi. p. 25.

§ Phil. Mag. July 1911.

slope of the tangent at any point is λ . By this graphic method it is easy to see whether λ is constant, when the line is straight; or whether λ decreases with the distance, indicating that the more easily absorbed rays are rapidly eliminated.

This method has been used by one of us* to determine the coefficient of absorption by air of the β rays from radium B and radium C, and from the active deposit of thorium. And this method has subsequently been adopted by Hess† in an important and remarkable experiment. A Wulf electrometer was used to measure the γ rays from radium C from 1400 mgs. of pure RaCl_2 , over ranges from 10 to 90 metres. The results obtained varied from $\cdot 389$ to $\cdot 493$ times 10^{-4} with a mean value $\mu = \cdot 0000447$, agreeing well with McClelland's ratio of $\mu/\text{density}$ for various elements and for water.

The present paper consists of an account of the application of the method, described above, to the determination of the coefficient of absorption of the Röntgen rays by air. Two electroscopes were used, the one fixed, the other moved to various distances. They were of simple type, with aluminium leaf, a capacity about 3 cm., and of considerable volume, 12 litres. Because Röntgen rays are not emitted very steadily from the source, it was necessary to compare the readings of the moved with a fixed electroscope as standard. It is not necessary to know either capacity or volume, only the potentials corresponding to the microscope-scale readings. In every case much scattered radiation reached the electroscopes from the air, roof, floor, and walls. It is, however, easy to determine the magnitude of this by placing a thick lead screen of size just sufficient to prevent any primary rays reaching the electroscope. The screen was placed at a distance of one to two metres from the electroscope. The scattered radiation was from 25 to 50 per cent. of the total, according to the experimental conditions; the ionization due to the scattered radiations was in all cases subtracted from the total radiation, so as to obtain the ionization in the electroscope due to rays coming from the direction of the source.

Short Ranges (4–10 m.).

At one end of a room 12 metres long was placed the Röntgen-ray bulb connected with a powerful induction-coil, with Wehnelt interrupter. The fixed electroscope was 6 m., and the moved electroscope at one of the stations 4, 6, 8, or 10 m., from the source. Measurements were taken both retiring and advancing, in order to eliminate the risk of

* Phil. Mag. July 1911.

† Phys. Zeit. 15 Nov. 1911.

error due to a change of hardness of the bulb. The current was passed for a few seconds and the fall of potential in each electroscope observed. The ratio (moved/fixed) was multiplied by the square of the distance between electroscope and bulb. The corresponding value for the scattered radiation was deducted, and the natural logarithm of the difference was plotted against the distance. The result for ranges of 4-10 metres gave a straight line, so that the rays obeyed the inverse square law and were also absorbed exponentially.

Three Röntgen-ray bulbs were used. The first (A) was an exceedingly hard one, used by one of us * some years ago in a comparison of the ionization of gases by Röntgen and γ rays. On the first day λ was found to be $\cdot 00077$ in the morning and $\cdot 00069$ in the afternoon; on the following day $\cdot 00065$. On the third day the bulb was run for some time, and the alternative spark-gap extended to a maximum of 30 cm. The bulb became extremely hard, and gave $\lambda = \cdot 00033$ in the morning and $\cdot 00025$ in the afternoon. These values accord well with those found for a very hard bulb by Rutherford and McClung, namely $\cdot 000279$. The rays from such bulbs are too penetrating to give good results for skiagrams for medical work.

The second bulb (B) tested was a new one, recently purchased by the Physics department. It was fitted with a regulator for varying the hardness, and it proved to be remarkably steady. Values in the morning and afternoon of the same day gave $\lambda = \cdot 00040$ and $\cdot 00041$. The alternative spark gap was 11 cm.

The third bulb (C) was the property of the Royal Victoria Hospital, and was too soft for medical work. Three determinations gave in succession $\cdot 0018$, $\cdot 0011$, $\cdot 0010$, and in the meantime the alternative spark-gap had increased from 1.5 to 5 cm. No satisfactory exact relationship was established between the length of the maximum alternative spark-gap and the value of λ .

A fourth bulb was examined, but although fitted with a regulator, it was extremely erratic, alternating between extreme hardness and softness, so that no reliable results could be obtained.

As the second bulb (B), $\lambda = \cdot 00044$, gives excellent shadow pictures, it would seem to be a good value for the coefficient of absorption for apparatus for medical work.

Long Ranges (20-80 m.).

The hard bulb (A) was placed on a ledge outside a window of the Physics building, 5 metres from the ground. The

* Phil. Mag. Nov. 1904.

fixed electroscope was placed on a table 40 m. from the source, and the stations for the movable electroscope were in a straight line at 20, 40, 60, 80 metres from the bulb, out of doors, on the College Campus.

The values obtained were :

Metres.	λ .
20-40	·00027
40-60	·00014 (?)

This bulb had given a mean value ·00029 within the building. Just as the readings at 60 m. were nearing completion, the bulb fractured near the cathode, and so there is some uncertainty as to the value of λ between 40 and 60 m.

On the day following the steady bulb (B) was used with results :

Metres.	λ .
20-40	·00040
40-60	·00029
60-80	·00010

This bulb had given within the building ·0004. The maximum alternative spark-gap was 11 cm.

The readings taken at the 80 m. station are not very accurate, for although the leaf was moving at the rate of 18 divisions a minute, there were troublesome convection currents due to a warm sun and a cold wind. The readings were taken in January, when there were 10 cm. of snow on the ground and the temperature was -6° C. Under suitable meteorological conditions it will be possible to take readings up to 150 m., and to decide whether there is really a decrease in the value of λ for increased distance as these results seem to indicate. This work we hope to undertake in the spring.

Total number of Ions.

If the number of ions produced in a cubic centimetre in a second is q , at a distance r from the bulb, we have

$$q = \frac{k}{r^2} e^{-\lambda r},$$

and the total number of ions produced in a second is

$$N = \int_0^{\infty} 2\pi r^2 dr \frac{k}{r^2} e^{-\lambda r} = 2\pi k / \lambda.$$

The constant k is the (theoretical) number of ions produced in 1 cubic centimetre at 1 centimetre distance from the focus on the anticathode.

The electroscopes were calibrated by the ionization due to

the γ rays from the radium C in a known quantity of radium bromide* at a measured distance from the electroscope †.

Now at a distance of 40 m. the hard bulb A produced 2340 ions per cubic centimetre per second; hence

$$2340 = \frac{k}{(4000)^2} e^{-.00029 \times 4000}$$

Therefore

$$k = 1.17 \times 10^{11},$$

and

$$N = 2\pi k/\lambda = 2.54 \times 10^{15}.$$

For the bulb B at 40 metres

$$k = 2.14 \times 10^{11},$$

$$N = 2.36 \times 10^{15}.$$

These values for N were found by integration over a hemisphere. As a comparison, it may be pointed out that, integrated over a sphere, the total number of ions per second, due to a gramme of radium, with RaC in equilibrium, is 1.1×10^{15} .

The power supplied to the Röntgen-ray bulbs was of the order 100 watts or 10^9 ergs per second. As the energy required to make an ion is about 2×10^{-11} erg, it follows that the power spent in ionizing is $2 \times 10^{-11} \times 2.4 \times 10^{15}$, or about 5×10^4 ergs per second. This is only 1/20000 part of the power passing to the bulb, the greater part of which is transformed into heat. The whole apparatus of induction-coil and bulb is exceedingly inefficient as a producer of Röntgen rays, which are, as it were, a minute side product.

If the ionization is integrated to the surface of the bulb instead of to the anticathode, the correction is less than 1 per cent.

Summary.

- (1) The coefficients of absorption by air have been found, at short ranges (4–10 m.), as follows :—

Soft bulb (C), .0018 to .0010.

Moderate bulb (B), .0004.

Hard bulb (A), .00033 to .00025.

These values agree well with previous determinations by Rutherford, and by Rutherford and McCllung.

* Phil. Mag. Sept. 1906 and Oct. 1911.

† It will be necessary, for more accurate determinations, to investigate the influence of the thickness and material of the walls of the electroscope on the internal ionization, and to compare the values obtained with those found for a very thin-walled electroscope. This question has received attention for γ rays (Phil. Mag. 1911, p. 30 and p. 554) but not apparently for Röntgen rays.

(2) For long ranges (20–80 m.) the values found were :

m.	B.	A.
20–40	·00040	·00027
40–60	·00029	·00014 (?)
60–80	·00010 (?)	

(3) The scattered radiation which has been deducted is from one-third to one-half of the primary.

(4) The total numbers of ions produced in the atmosphere per second were found to be (A) $2\cdot54 \times 10^{15}$; (B) $2\cdot36 \times 10^{15}$. The energy spent in ionizing is, therefore, only about 1/20000 of that expended in the bulb.

We are indebted to Mr. L. V. King for his kind assistance in the long range measurements.

LXVI. *Non-Newtonian Mechanics.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

THE defence which Dr. Tolman, in the last number of the *Phil. Mag.*, sets up against my criticisms is strange indeed. He points out that his argument, even after I have restated it in a form free from certain logical absurdities, still contains an error. I readily admit the fact, but the error is his, not mine; it is contained in his original argument, which I was concerned to correct only in one point and for which I have not accepted the smallest responsibility.

Apparently he now admits that the argument was insufficient, for in the revised form which he now puts forward he introduces an additional assumption. To the assumptions of the conservation of momentum and the Einstein space-time transformation, he adds that of the conservation of mass, which is not deducible from them alone. The work of Epstein (*Ann. d. Phys.*, xxxvi. p. 793) seems to show that the additional assumption is unnecessary.

In a footnote Dr. Tolman attempts to refute my main criticism by a defence which I answered in the last paragraph of my attack. I pointed out that arguments which are legitimate in making deductions from general principles are not always legitimate in establishing these principles. I see no reason to withdraw my assertion that the application of the principle of conservation of momentum to cases (such as that of the Bucherer experiment) where the observer is situated on one of the reacting systems is inconsistent with the principle of relativity.

I am,

Yours faithfully,

Leeds University,
March 3, 1912.

NORMAN R. CAMPBELL.



FIG. 4.

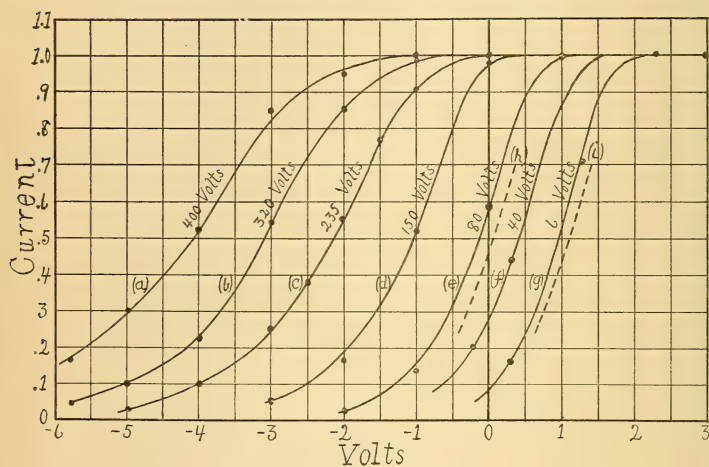


FIG. 5.

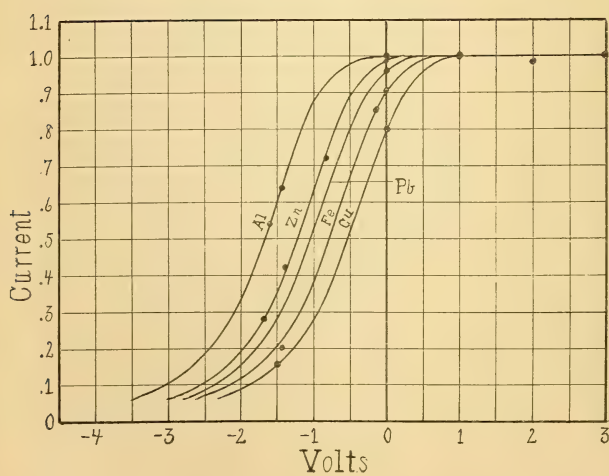


FIG. 6.

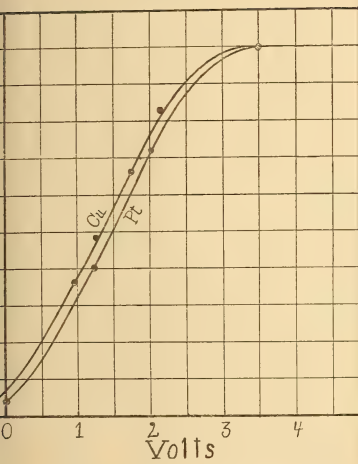


FIG. 7.

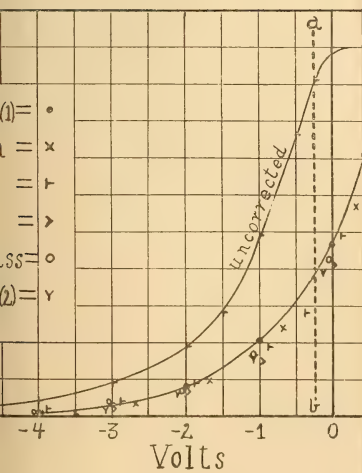


FIG. 4.

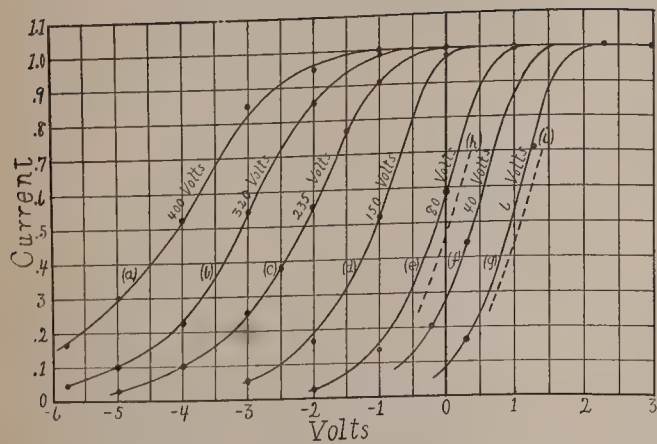


FIG. 6.

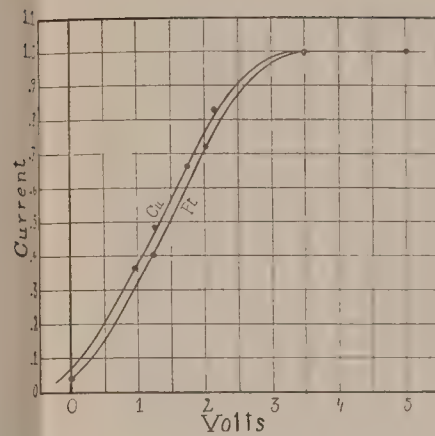


FIG. 8.

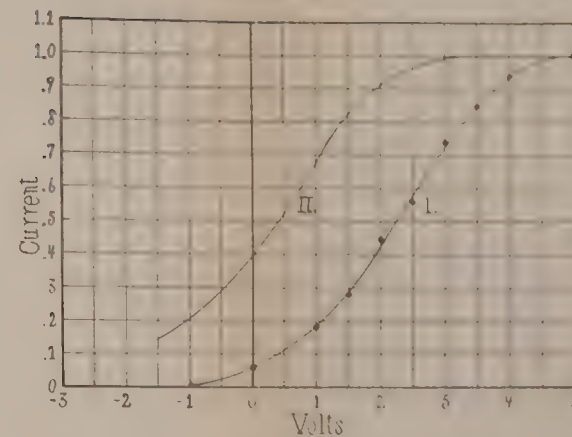


FIG. 5.

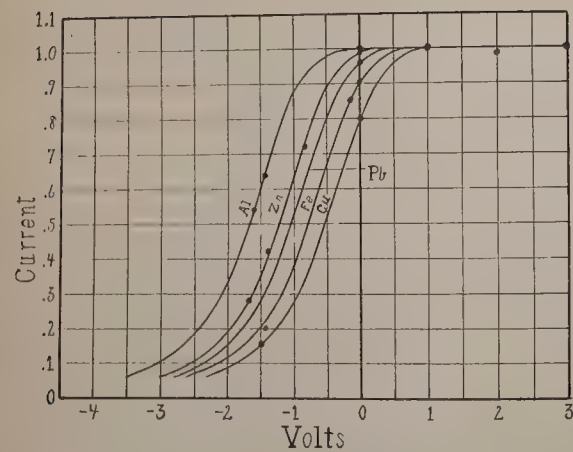


FIG. 7.

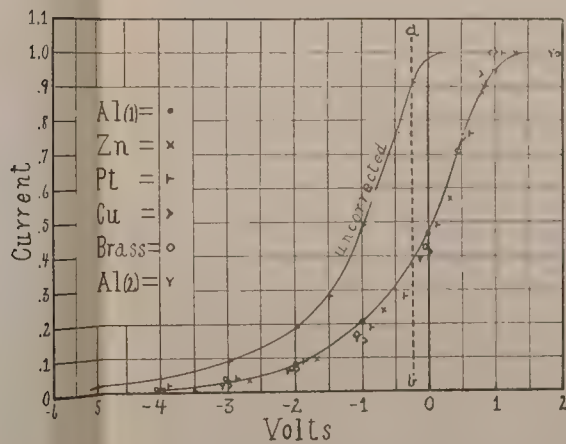
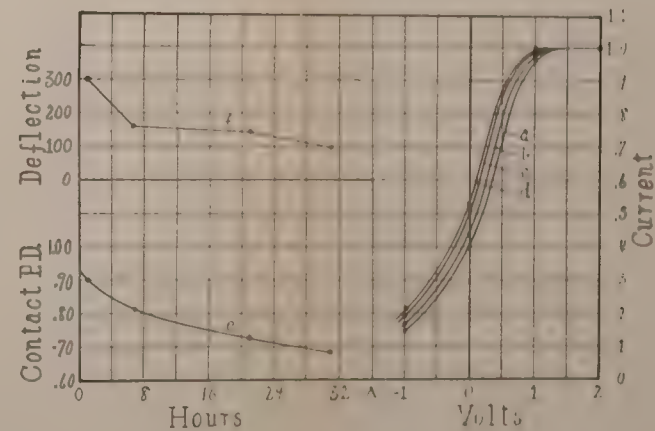
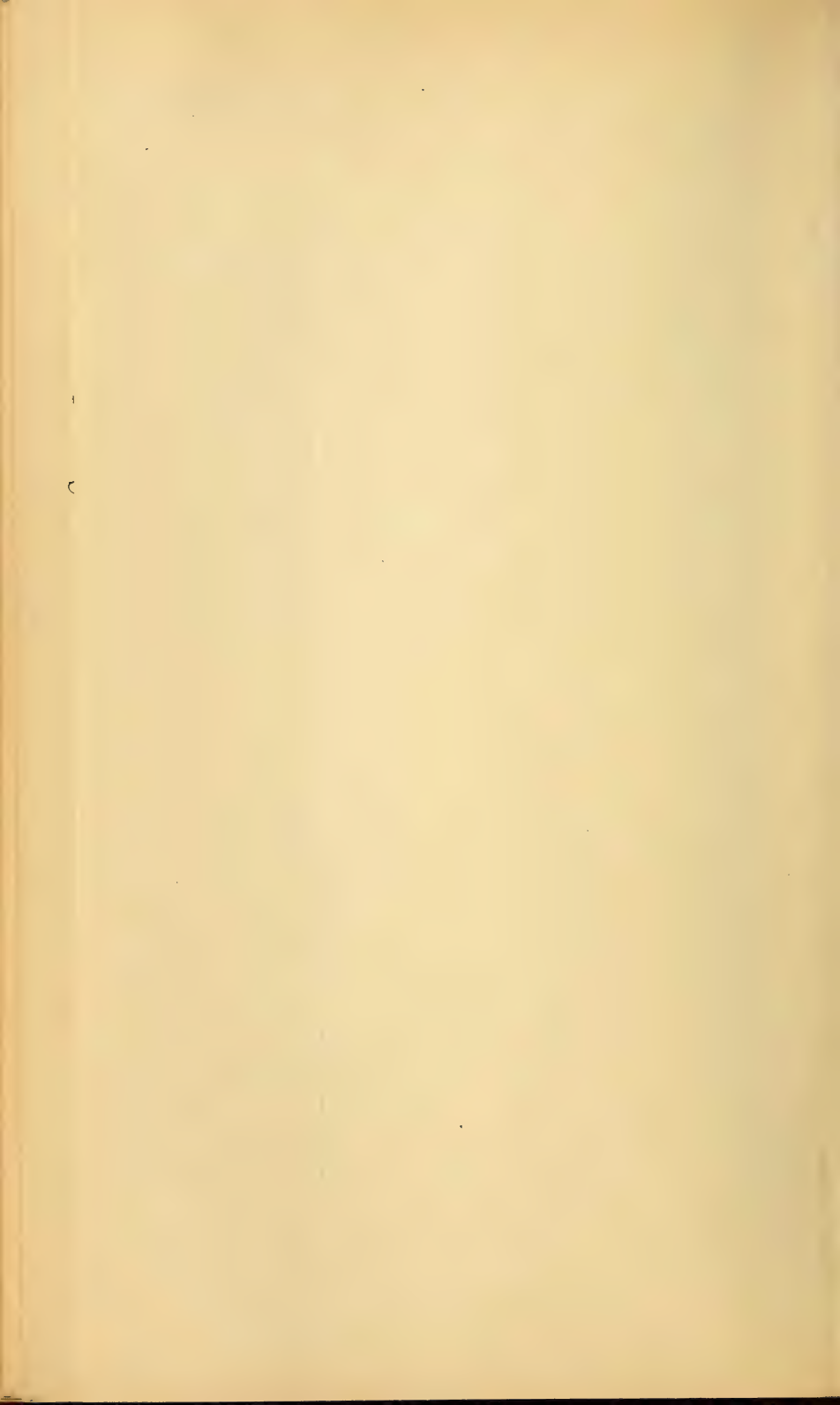


FIG. 9.





THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

MAY 1912.

LXVII. *Selective Reflexion, Scattering and Absorption by Resonating Gas Molecules.* By R. W. WOOD, Professor of Experimental Physics, Johns Hopkins University, and Adams Research Fellow of Columbia University*.

[Plates X.-XII.]

IN the present paper I shall deal with phenomena which, up to the present time, have never been made the subject of experimental investigation; and though elaborate mathematical treatments have been given by Planck, Lord Rayleigh, Schuster, Lamb, and others, no experimental data have ever been obtained. Through the discovery that the vapour of mercury, at room temperature, emits a brilliant resonance radiation when stimulated by monochromatic ultra-violet light of wave-length corresponding exactly to that of its so-called absorption line ($\lambda=2536$), I have been enabled at last to obtain quantitative data on the subject.

It has been found that when the vapour is in a high vacuum there is no true absorption, the energy diverted from the primary beam of light being wholly scattered, as imagined by Planck in his treatment of the theory of absorption. The presence of a small quantity of air or other gas has been found to introduce the factor of true absorption, or the conversion of the energy of the light-waves into heat, and the ratio of the amount of energy scattered to that absorbed as a function of the pressure of the gas with which

* Communicated by the Author.

the mercury vapour is mixed has been determined. A very remarkable secondary resonance radiation of the gas not directly illuminated by the primary beam, but stimulated by the light which comes from the directly excited molecules, has been discovered, the study of which has enabled me to draw the conclusion that there is no true absorption except when the pressure is raised by the presence of air.

I have also succeeded in passing by gradual stages from the condition in which the resonance radiation is diffusely scattered to that in which, owing to the proximity of the molecules, it is regularly reflected from the surface of the gas mass. A resonance lamp has been constructed which emits light probably more homogeneous than that obtained from any source hitherto known, by the light of which I have succeeded in photographing the vapour rising from a drop of warm mercury into the air of the room like black smoke. So sensitive is the light of this lamp to the presence of mercury vapour, that I have been obliged to ventilate my room before each experiment, owing to the presence of mercury in the cracks on the floor, for the light of the lamp is reduced to one-half of its intensity by traversing a layer of mercury vapour at room temperature only 5 mm. in thickness.

The following topics will be discussed :—

Introduction.

Resonance radiation of mercury vapour at room temperature.

Energy diverted from the primary beam.

Primary and Secondary Resonance Radiation.

Destruction of the Secondary Radiation by molecular collisions.

Probability that the molecules continue to emit light after they leave the region traversed by the primary beam.

Ratio between Scattered and Absorbed Light as a function of the pressure of the gas.

Transition from Diffuse Scattering to Regular Reflexion.

Absence of all traces of Polarization.

Experiments with the Resonance Lamp.

Introduction.

The scattering of light by gas molecules has been the subject of mathematical treatments, but practically no experimental work has been done upon the subject, and we have no data whatever regarding the actual amount of energy

diverted from the primary beam by a molecule in exact resonance with the light-waves which excite it.

Lord Rayleigh has interested himself chiefly with the scattering which may occur when the molecules are not in resonance, as is the case in the scattering of the blue light by the molecules of the atmosphere. This case has been experimentally investigated by Abbott, who has measured the atmospheric absorption from the summit of Mount Wilson. Of greater interest, however, is the scattering of molecules resonating under the influence of the light-waves. But few cases of this are known, though this action has been made the basis of the theory of absorption developed by Planck. Some years ago I found that the non-luminous vapour of sodium at a comparatively low temperature, when illuminated by the light from a powerful sodium flame, re-emitted light of the same wave-length in all directions. This re-emission of light, without change of wave-length, by molecules of an absorbing gas, I named resonance radiation, to distinguish it from fluorescence, where there is in general an increase in the wave-length. Sodium vapour is, however, almost impossible to handle in a satisfactory manner, and is in consequence unsuitable for a quantitative investigation of the subject.

About two years ago I discovered that mercury vapour acts in the same manner, except that the phenomenon occurs in the ultra-violet region at the absorption line 2536. I first observed the resonance radiation of this vapour at room temperature in an exhausted silica bulb, the pressure of the mercury vapour being 0.001 mm.

This vapour appeared to be the ideal medium for a careful study of the subject in all of its aspects, except for the fact that everything has to be done by photography. The work has turned out even better than I had hoped, and I have been able to pass gradually from the case where the scattered light is radiated in all directions by the highly rarefied gas to that in which it is regularly reflected from the surface of the gas under high pressure.

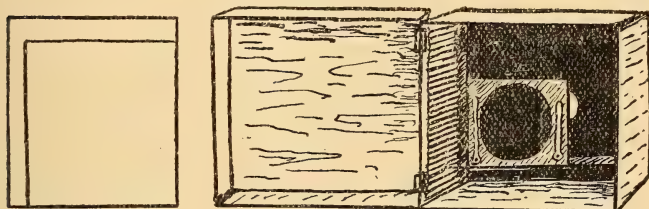
I have already described the selective reflexion of monochromatic light by mercury vapour (this journal, vol. xviii. p. 187, 1909), in a paper which I shall have occasion to refer to later on.

Although I first observed the resonance radiation of mercury vapour nearly two years ago, I published nothing on the subject, as no quantitative data had been obtained. The observation was made in the following way. A small drop of mercury was introduced into a tube of fused quartz,

closed by end plates of the same substance which had been ground flat and polished. These plates were fused to the ends of the tube, which had been flared out in order to prevent spoiling the figure of the central portion of the plates by fusion. The tube is shown in Pl. X. fig. 1, and was designed for a study of the dispersion of the vapour by an interferometer method, an investigation of which will shortly be commenced. It was made by Heraeus and turned out quite as well as I had hoped, for I have had no difficulty in forming interference fringes with one beam of light traversing the tube, showing that the process of fusing on the end plates did not damage their optical quality. The tube was highly exhausted and sealed, and the light of a quartz mercury arc focussed along the axis of the tube. The tube was now photographed from the side with a camera furnished with a lens of quartz, which was constructed in a few minutes from an old box used for storing photographic negatives. A quartz lens of about 18 cm. focus was fitted into a hole made in the bottom of the box, which was used standing on its side. A strip of thick sheet brass was cut to the same width as the plates for which the box was made. To this strip was soldered another strip in which a circular aperture 8 cm. in diameter had been cut. This strip stood vertically in the box, and was provided with two spring clips, or supporting clamps, to hold the plate in place against the circular aperture. The camera was focussed by sliding the strip along in the grooves which supported it. (These grooves were made originally for holding the plates.) The correct focus for the invisible rays with which we are concerned in the present paper was found by pointing the camera at the slit which had been mounted in the focal plane of the quartz spectrograph (to convert it into a monochromator), and observing the focus with a piece of uranium glass. The distance from the lens to the slit from which the ultra-violet rays diverged was then measured. This gives the correct distance at which the object to be photographed must be placed in order to be properly focussed. The camera is shown in fig. 1 *a*. I have found that much time is saved by the use of a camera of this description, for the plates can be cut carelessly and in a hurry, as they do not have to be of an exact size, and no time is lost in loading or unloading a plate-holder. In ultra-violet work of this description, where the sources of error and all other unexpected troubles and difficulties have to be located by photography, the time saved in this way amounts to a good deal. In the present work I have taken about six hundred

photographs, and have saved the many hours that would have been spent in fussing with plate-holders and miss-fit plates. The hinged back of the box can be swung aside and the plate inserted in the supporting clamps in a few seconds, the room being darkened of course.

Fig. 1 a.



The Westinghouse quartz arc was enclosed in a box and the collimator of the quartz spectrograph introduced through a small hole. In this way diffused light, which would have spoiled everything, was shut out. The lamp was started by pulling a string which passed through a small hole in the top of the box, and extinguished at the right moment by opening a switch.

The monochromatic light from the slit of the quartz spectrograph was either made parallel, or brought to a focus by means of a pair of quartz lenses of 30 cm. focus each, the condition of the pencil of rays being tested with the uranium glass plate.

The photograph taken of the long tube closed with flat quartz plates showed an image of the cone of rays traversing the high vacuum precisely as if the tube were filled with dense smoke. The tube was at room temperature, and the density of the mercury vapour was about 0.001 mm., nevertheless an exposure of fifteen or twenty seconds was all that was necessary.

Owing to my absence from Baltimore I was unable to take up the work again until this winter. In the meantime I had secured a Westinghouse Cooper-Hewitt quartz mercury arc which was very much more powerful than my old Heraeus lamp. These quartz arcs emit the strong line of wave-length 2536, and it is this light alone which excites the resonance radiation.

To my surprise, on repeating the experiment of two years ago with the new arc lamp, I found no trace whatever of the luminous cone of light, even with an exposure of several minutes. On looking up my notes, however, I found that in

the earlier experiments I excited the lamp with a high potential current from a transformer, running it at a comparatively low temperature. It immediately occurred to me that in the present case I was working with the lamp at high temperature, and that the 2536 line was very likely reversed, the wave-length necessary for the excitation of the resonance radiation being removed by absorption. I accordingly allowed the lamp to become quite cold, and made my exposure when the lamp was first lighted, when its light is quite violet in colour. On developing the plate I found that a five seconds exposure gave me a more intense cone of light than anything that I had ever observed before. It was absolutely black on the negative. Moreover, the vapour outside of the cone of focussed rays appeared to be glowing at the end of the tube where the beam passed in. As the fused quartz is somewhat fluorescent under the action of the rays emitted by the lamp, it was necessary to prove that this light did not come from the walls of the tube. That such is not the case I shall show when we come to subsequent experiments.

A photograph of the resonance radiation in the tube is reproduced on Pl. XI. fig. 1.

It was next necessary to observe the spectrum of the light emitted by the mercury vapour, and the slit of a quartz spectrograph was opened wide and brought up close to the silica tube. Two photographs were made—the first of ten seconds exposure immediately on starting the Westinghouse lamp; the second, also of ten seconds after the lamp had been running half a minute. These photographs are shown in Pl. XI. fig. 2. In the second spectrum the broadened image of the slit is shown at the 2536 line (indicated), the other lines appearing narrow. These lines result from the circumstance that some direct light from the arc illuminated one of the jaws of the slit. The upper spectrum, taken after the lamp had been in action for half a minute, is identical with the second, except that the broad image of the slit is absent, showing that the resonance radiation has disappeared. I then made a series of four spectra taken one after the other. These showed that the resonance radiation was very strong during the first five seconds of the lamp's operation, quite faint during the second five seconds operation, the merest trace during the third five seconds, and completely gone in the next five seconds. In all of the subsequent work I accordingly allowed the lamp to become quite cold, and extinguished it after a run of exactly five seconds. This insured uniformity in the exposures. The slit of the spectro-

graph was now made as narrow as possible and five exposures were superposed of five seconds each, the direct light from the arc being screened from the slit. The spectrum showed only the 2536 line, exceedingly narrow and sharp, thus proving that we are dealing with a very beautiful case of pure resonance radiation. In fact, I suspect that this radiation will be found to be the most homogeneous which we have, for the vapour is not only at a lower pressure than is usual in vacuum-tubes, but *it is at room temperature*. In Pl. XI. fig. 2, the third spectrum is that of the resonating vapour, the fourth spectrum that of the mercury arc.

I next investigated the effect of raising the temperature of the tube which was mounted in a small air-bath. It was found, as was to be expected, that, as the temperature rose, the cone of emitted light became shorter and brighter, until it finally disappeared, the emitted light coming from the inner surface of the plate where the incident beam of light entered. As no especial significance is attached to the records obtained in this way, I shall postpone any further discussion of the effects of increasing the density of the vapour until I take up the subject of the transition from diffuse scattering of the emitted light to its recombination into a regularly reflected wave, which can be accomplished by increasing sufficiently the density of the vapour.

We will now take up the important subject of the amount of energy diverted from the incident beam by the resonating gas molecules.

Amount of Energy diverted from the Primary Beam.

It is clear at the outset that if we wish to determine the amount of energy diverted by the resonators when they are in exact synchronism with the light-waves, it is useless to make observations upon the intensity of the light after it has suffered transmission through the vapour, even if we are dealing with what we are accustomed to call monochromatic light. All spectrum lines have a finite width, and the particular frequency scattered by the resonating molecules may constitute but a small fraction of the total energy of the spectrum line used to excite the vapour; in other words, it is only the centre of the line that is effective in exciting resonance, the edges of the line not being reduced in intensity by the transmission through the gas. What we wish to determine is the reduction in intensity of that portion of the line, or in other words the frequency, which is capable of exciting the natural period of vibration of the

molecule. It appeared to me that the most direct way of investigating this question was to take the intensity of the cone of light as the measure of the intensity of the primary beam, for there appears to be no doubt but that the intensity of the resonance radiation is proportional to the intensity of that particular frequency in the exciting light which is capable of setting up resonance. I accordingly made a very large number of photographs with different times of exposure and different vapour densities, and measured the photographic density of the image at different distances from the point where the light entered the vapour. This gives us a measure of the rate at which the vapour cuts down the amplitude of the exciting frequency as the wave moves through the medium. The method by which these measurements were made will be described presently, and for the present I need only point out that the usual precautions necessary in photometric work by photography were taken. The mercury vapour in this case was not contained in the quartz tube, for it was impossible to get a good image of the excited region close up to the point at which the beam entered on account of the irregular refraction by the wall of the tube. A rectangular box of brass with windows of crystal quartz plates, which I shall describe presently, was used, and by paying attention to adjustments, it was possible to get beautifully sharp images of the excited region close up to the surface of the window through which the light entered. I made measurements on fully a dozen plates taken on different days, and found that the intensity of the primary beam was reduced to one-half of its value after travelling for a distance of 5 mm. in mercury vapour at a pressure of 0.001 mm. The smallest value found was 4 mm. and the largest 6 mm. for a reduction to half intensity, a variation due without doubt to the circumstance that the room temperature varied by several degrees from day to day. This variation in the temperature of the room was just about sufficient to account for the slight differences observed, and we can safely assign the value of 5 mm. for a temperature of 22° C. Measuring the intensity along the path of the beam it was found that the ordinary law of absorption was very closely followed, *i. e.* a 10 mm. layer reduced the intensity to $1/4$, and a 15 mm. one reduced it to $1/8$ of its original value. It appeared to me, however, that the reduction of the intensity did not follow this law exactly, but that the intensity was a trifle greater after 15 mm. had been traversed than the intensity calculated on the assumption that every

5 mm. effected a reduction of $1/2$. This is in agreement with a calculation made by Schuster in his paper on "Radiation through a Foggy Atmosphere" (Astrophysical Journ. vol. xxi. p. 6, 1905), though the differences in this case are not much larger than the probable errors in the measurements. The beam of light which entered the cell was made accurately parallel by means of a quartz lens and passed through a square aperture (measuring 5 mm. on a side) perforated in a black card. In this way a beam of uniform cross-section was obtained, which was of course necessary if the measurements were to be of any value. Only the ultra-violet 2536 light entered the cell, a quartz spectrograph being used as a monochromator.

We are now in a position to consider the amount of energy diverted from the primary beam by each molecule.

Lamb, in his theoretical treatment of the absorption of light by a gas, published in the Stokes Commemoration of the Camb. Phil. Soc., sums up a calculation in the following words:—"Hence in the case of exact synchronism, each molecule of gas would, if it acted independently, divert per unit of time nearly half as much energy as in the primary waves crosses a square whose side is equal to the wave-length." This means, if I am not mistaken, that if we had a density such that there was one molecule in each cube the sides of which were equal to the wave-length, the intensity of the light would be reduced by $1/2$ by traversing a single layer of molecules, while a density ten or twenty times as great as this ought to give selective reflexion, since the wave would be practically stopped before penetrating to a depth of more than a small fraction of a wave-length.

Let us now compare this calculation with the values which have been determined. At a pressure of 0.001 mm., which is about the pressure used, the average molecular distance is such that we shall have on the average one molecule of mercury in every cube the sides of which are only very little larger than the wave-length (or more exactly 0.0003 mm.), which quantity divided into 5 mms., the distance traversed for a reduction of intensity equal to $1/2$, gives us 16,000, that is to say 16,000 molecules must be passed before one half of the energy is removed from a square element on the wave-front measuring λ on each side.

Of course this calculation is made on the assumption that all of the molecules are equally effective in scattering the light. It is however possible, even probable, that but a small percentage are, at any given moment, in the condition

to act as resonators. Experiments on the dispersion and magnetic rotation of metallic vapours and luminescent hydrogen give evidence that but a small percentage of the molecules are at any instant concerned in the production of the phenomena in question.

Primary and Secondary Resonance Radiation.

Photographs of the luminous cone of mercury vapour at room temperature contained in the quartz tube appeared to prove that the vapour outside of the cone of vapour directly excited by the primary beam was itself luminous. It was observed, however, that the fused quartz phosphoresces with a violet light under the influence of the ultra-violet light, and I did not feel perfectly sure that the light did not come from the wall of the tube. To eliminate such a possibility a hollow box of brass was constructed (Pl. X. fig. 2), two adjacent sides of which were left open, and closed with thin plates of quartz (crystal) which is not phosphorescent. The inside of the box was heavily smoked, and the plates cemented in place with sealing-wax. A drop of mercury was introduced and the interior of the box put in communication with a Gaede pump and exhausted. The ultra-violet light was focussed at the centre of the box, entering through one of the quartz plates, and the resonance radiation photographed from the side through the other plate. It was found that, unless the pressure of the air was less than three or four millimetres, no trace of any secondary radiation was present. On lowering the pressure of the residual air it developed rapidly however, and after the pump had been in operation for several minutes, the luminous glow filled the entire interior of the box, the luminous cone being nearly lost on the strongly luminous background. With correctly timed exposures the directly excited resonance radiation is always four or five times brighter than the secondary radiation. Over exposure may, however, increase the effect of the secondary until it equals that of the primary, causing the outlines of the primary beam to disappear almost completely, as in the first picture in fig. 4, Pl. XI.

The intensity of the secondary radiation depends upon the cross-section of the primary beam, as does also the rate at which its intensity diminishes with increasing distance from the primary rays. With an exciting beam of square cross-section (5 mm.²) the intensity of the secondary radiation half a millimetre from the edge of the beam was found to be

nearly $\frac{1}{3}$ of the intensity of the adjacent primary radiation. Its intensity fell off with increasing distance as follows :—

Distance.	Ratio.
0.5 mm.	1/3
1.5 „	1/6
2.5 „	1/10
3.5 „	1/30

Four photographs of the phenomenon are reproduced on Pl. XI. fig. 4. A vacuum-tube was put in circuit with the tube leading to the pump, to serve as an auxiliary manometer, and it was found that the secondary radiation did not appear in its maximum intensity until the green fluorescence due to cathode rays appeared in the vacuum-tube.

The arrangement of the apparatus is shown in Pl. X. fig. 2, which requires no explanation. It is clear from the photographs that when the mercury vapour is in the highest possible vacuum, the light which it emits is capable of exciting a secondary radiation in the surrounding vapour which lies wholly outside of the path of the primary exciting beam. The presence of air at 4 or 5 mm. pressure, while it materially decreases the intensity of the primary resonance radiation, causes the secondary radiation to disappear entirely. In the four photographs which are reproduced I have recorded the pressure of the residual air in each case. To make sure that the disappearance of the secondary radiation was not due to a weakening of the primary radiation, I gave an exposure of four times the normal one, with air at 4 mm., and though the cone was very much blacker on the plate than on any of the others, there was no trace of any luminosity in the surrounding vapour.

This action of a small trace of air is most remarkable, and it is of the utmost importance to determine the explanation. Although the vapour which is in the path of the primary beam glows with diminished brilliancy, the light which it gives out seems powerless to excite the surrounding vapour to luminosity. It seemed possible that the damping due to molecular collisions rendered the emitted light less homogeneous and therefore incapable of exciting the vapour, in spite of the fact that the absorption band must be regarded as broadened to a similar amount. This point is one which requires very careful investigation, and if the cause can be found much light may be thrown upon the nature of the effects of molecular collisions upon radiation. It occurred

to me that it might be possible that the emission of light by the vapour surrounding the primary cone might not be due to light emitted by the vapour directly excited, but to the circumstance that, owing to the great length of the mean free path, the mercury molecules might continue to emit light after flying outside of the limits of the primary beam. The action of a small amount of air in destroying the luminosity would follow at once as a result of the reduction in the length of the free path, the luminosity being destroyed by the collisions.

Probability that the Molecules continue to emit Light after they leave the region traversed by the Primary Beam.

Fortunately this is an hypothesis which is very easily tested by experiment, for we have only to divide the cell into two compartments by means of a partition of quartz, passing the exciting beam immediately below and close to the under side of the horizontal partition. The partition will stop the moving molecules, but will transmit the light emitted by the vapour illuminated by the primary beam. A small plate of quartz 1.5 mm. in thickness was cemented to the front window of the cell as shown in Pl. X. fig. 3, and the cell exhausted until nothing but the green phosphorescence was visible in the discharge-tube. The resulting photograph showed that there was considerable luminosity in the upper chamber, but it appeared to be of somewhat less intensity than that of the vapour in the lower chamber. The photograph, however, was not very satisfactory owing to the thickness of the partition. The cell was accordingly made over again, with a partition consisting of a quartz plate only $\frac{1}{4}$ mm. in thickness, and the same phenomenon was found, somewhat greater intensity of the secondary radiation in the compartment traversed by the exciting beam. Calculation of the reflecting power of the quartz plate from its refractive index for the wave-length in question showed that a reduction of intensity of 10 per cent. was to be expected from this circumstance, but this did not seem to be sufficient to explain the observed diminution of the intensity; and careful measurements of the intensity of the secondary radiation at equal distances from the centre of the primary beam were made by comparison with a plate exposed in strips by gradually increasing amounts of time, which was developed with a photograph of the cell for exactly the same length of time. These measurements showed that the effect of the thin partition was to reduce the

intensity of the secondary radiation by an amount varying from 25 to 30 per cent. This appears to be very strong evidence of the persistence of the luminosity of the molecule after it leaves the region traversed by the exciting beam. Direct evidence of the phenomenon is much to be desired, but I have been unable to think of any method, for we cannot make a screen which will transmit the moving molecules but cut off the light.

It is evident, however, that the primary cause of the destruction of the intensity of the secondary radiation by the presence of air at three or four millimetres pressure is to be sought elsewhere, as fully 75 per cent. of the secondary radiation results from the light of the primary. I shall now show that the effect of the air in reducing the intensity of the secondary radiation results from the introduction of the factor of true absorption as contrasted with molecular scattering.

Molecular Scattering and True Absorption.
Ratio of the two quantities.

It is easy to see that, if true absorption occurs as well as scattering, the intensity of the secondary radiation will be greatly diminished in intensity. When the vapour is in a vacuum of less than .01 mm. it is probable that the energy diverted from the primary exciting beam is all scattered, and no true absorption occurs. We should of course find what appeared to be an absorption line in the spectrum of the transmitted light, and yet the molecules would not be absorbing energy but merely diverting it from the primary beam and sending it out in all directions. The molecules lying in the path of the beam will glow with a certain intensity, while those which lie outside of the path of the beam will be illuminated by the radiating molecules which are directly excited, and will in consequence emit a light of a lesser intensity. Suppose now that by the introduction of air at a pressure of 5 mm. the intensity of the light emitted by the directly excited molecules is reduced to $\frac{1}{3}$ of its original value. By means of a threefold increase in the intensity of the exciting light we can raise this intensity to its original value, so that the same amount of light is available for the excitation of the secondary radiation as before. The intensity of the secondary radiation excited under these circumstances will, however, be only one-third of its former value, since two-thirds of the energy received from the directly excited molecules is transformed into heat by the true absorption which has been introduced by the

presence of the air. The intensity of the secondary resonance radiation in comparison with that of the primary will consequently be much less (one-third) than when the mercury vapour was in a high vacuum. This hypothesis was tested by experiment and practically proven. In the first place a very careful series of measurements was made of the reduction in the intensity of the primary resonance radiation by the introduction of air. The pressure of the air was measured with a McLeod gauge, and the duration and intensities of the excitation were made as nearly equal as possible.

The exposures were all made on the same plate, which was pushed along in the supporting clamps, the mercury lamp being allowed to cool down completely between exposures. To insure against accidental errors, a large number of plates were exposed, and the measurements made from each were compared. One of these plates is reproduced on Pl. XI. fig. 12. The air pressure in the cell is marked on each picture. The exciting beam enters the cell from the right, and two thirds of the quartz window was screened off, so that a number of exposures could be made on the same plate. In the first picture (pressure 0.01 mm.) the secondary radiation from the region not excited by the primary beam is very conspicuous, less so in the second and nearly gone in the third. The intensities of the primary radiation at the point where the incident beam entered the cell was measured by comparing the density of the negative with the density of a plate exposed in strips for times increasing gradually from 5 to 300, which plate was developed simultaneously with the other. The comparison was made in a very simple way which, with practice, was susceptible of considerable accuracy. A clean cut was made with a sharp knife through the film on each plate, perpendicular to the direction of the strips on the comparison plate, and through the region at which the density was to be measured on the other plate. The film was removed along one side of the cut in each case, exposing the clear glass. The two plates were now placed in contact film to film, and the comparison strip slid along until a perfect density match was made with the photograph, the dividing line between the two disappearing. In practice it was found advantageous to cover the plates with a black card perforated with a small rectangular aperture, which was brought over the region under investigation, and the best match could be made by throwing the eye a trifle out of focus, thus causing the very narrow line separating the two halves of the field to disappear.

The values found are given in the following table.

Air pressure in mm.	Intensity of primary resonance radiation.	Absorbed energy.
·01	300	0
·45	230	70
1·10	200	100
2·20	170	130
6·20	100	200
9·50	70	230
14·20	50	250
18·00	40	260
32·00	12	288

If we plot these values, taking intensities as ordinates and air pressures as abscissæ, we obtain a curve practically identical with the curve obtained with iodine vapour, which shows that the effect of the air upon the intensity of the emitted radiation is about the same in the two cases. In the third column I have given the amounts of the energy absorbed in each case. These values are merely the differences between the amounts of the emitted energies and the energy emitted when the vapour is in a high vacuum (300), and are calculated on the assumption that the total energy diverted from the primary beam is the same in the two cases, *i.e.*, that the presence of the air does not influence the amount of energy removed from the beam by the resonating gas molecules.

That this is in reality the case was shown by the following experiment. A double cell, Pl. X. fig. 4*b*, was made by soldering a cross partition along a diameter of a short section of large brass tube, the ends of which were closed with quartz windows. The length of the tube was 17 mm., and the diameter 30 mm., and two small brass tubes permitted either compartment to be exhausted to any desired pressure. In measuring the energy diverted from the primary beam by the vapour, we must be certain that we use light which is in exact synchronism with the resonating molecules. The light must be far more homogeneous than the ray isolated by the quartz spectrograph from the light of the mercury arc. I used therefore what I shall hereafter refer to as the resonance lamp, a small quartz bulb, closed at the bottom with a flat plate of polished fused quartz, which was fused on in the same manner as the end plates of the long tube previously described. This bulb contained a drop of mercury, and was highly exhausted and sealed. The light from the quartz spectrograph

was focussed through the side of the bulb as close to the centre of the flat bottom as possible. The adjustments were made by means of a small piece of uranium glass, which enables one to locate the path of the rays by its phosphorescence. It is most important to prevent the light which is reflected from the walls of the bulb from getting at the photographic plate. This gave a good deal of trouble, but by means of the device shown in Pl. X. fig. 4 *a*, it was practically eliminated. A wooden box was made, measuring $40 \times 10 \times 10$ cm., and a large circular hole cut in one end which was covered with a cone of black cardboard made by cutting out a circular disk, cutting along a radius and pasting the cut edges together, overlapping them about 2 cm. A small round hole was burned through the apex of the cone, and this was placed against the flat bottom of the resonance lamp. A quartz lens mounted in a partition of the box rendered the rays which came from the resonance lamp through the small hole parallel, so that the intensity of the light after its passage through the cell could be recorded close to the cell or at a distance from it. The importance of doing this is apparent from the following considerations. If we place a photographic plate close against the double cell containing the vapour, it will be illuminated by the primary beam which has traversed the cell and also by the scattered resonance radiation. If, however, we place the plate at a distance, say at the other end of the box, the primary rays, being parallel, will reach it with undiminished intensity, while the effect of the scattered radiation will be negligible, since its intensity diminishes according to the law of inverse squares. No difference should be found with the plate in the two positions for the light which has gone through the compartment containing air and mercury vapour, since, as we have seen, the presence of the air destroys the resonance radiation. The experiment was made in the following way. One compartment of the double cell was highly exhausted and the other to a pressure of 3 cm. A strip of photographic plate 1.5 cm. in width was mounted close to the cell and received the light which had traversed the lower half of each compartment. A larger plate was mounted at the other end of the box, and received the light which passed above the first plate, and had traversed the upper halves of the compartments. Thus four records were obtained at once under precisely similar conditions as regards exposure-time and development. Much trouble was experienced in getting things adjusted so that the intensity close to the lens and at the end of the box came out the same with the cell removed, which is of course a necessary preliminary experiment. It was finally found that the air of

the room contained enough mercury vapour to reduce the intensity of the light from the resonance lamp by nearly one half as it traversed the length of the box.

This is not so surprising when we remember that the earlier experiments showed that the primary beam was reduced to one half of its intensity (*i.e.*, the frequency capable of exciting resonance was) by traversing 5 mm. of the saturated vapour at room temperature. The trouble was overcome by opening the windows and thoroughly ventilating the room before each experiment. One is reminded of the trouble experienced in carrying on certain investigations in laboratories which have become infected by radium!

One of the photographs obtained with the double cell is reproduced on Pl. XI. fig. 3. In this case one compartment was free from mercury vapour, while the other contained it. This particular cell was, however, only 8 mm. in thickness, and gives a good idea of the powerful absorption of the highly homogeneous light from the resonance lamp by a shallow layer of the vapour at room temperature. The other photographs showed that the energy diverted from the primary beam was the same for mercury in a high vacuum and in air at 3 cm. pressure, so that the calculation of the absorption-scattering ratio which I gave provisionally was justified.

It was found, however, that if air at atmospheric pressure was admitted to one compartment the absorption was decreased by more than one half. This is just the opposite of what I found three years ago, when I discovered that I could photograph the 2536 absorption line by passing the light of a cadmium spark through a tube 3 metres long containing mercury vapour at room temperature, if the tube contained air at atmospheric pressure, while no trace of the line appeared if the tube was exhausted. There is, however, no real discrepancy, for the effect of the air, as I have shown previously, is to broaden the absorption line. This circumstance was discovered independently by Ångström in the case of CO_2 . The present experiments appear to show as well that, while the line is broadened, the intensity of the absorption at the centre of the line is materially reduced. I have observed the same thing with iodine vapour, the lines becoming fuzzy and less black when air is admitted to the tube.

The failure to obtain the absorption line in the earlier experiment with the three-metre tube exhausted was of course simply due to the insufficient resolving power of the spectrograph employed.

In the experiments with the double cell which I have just described, I was unable to find any distinct evidence that

the resonance radiation contributed to the darkening of the photographic plate, for there appeared to be no difference between the case of a plate placed close against the cell and one placed at a distance. There is reason to believe that the radiations emitted by a resonator lag in phase behind the phase of the primary wave by 180° , that is they should reduce the intensity of the primary wave by interference. This is a delicate matter to investigate experimentally, but I have made one or two attempts. If we place a black screen perforated with two small holes in front of the cell, we can limit the radiation which traverses the cell to two beams of small cross-section, each compartment transmitting one of them. The primary wave will now record itself on the plate as two small spots of the same diameter as that of the apertures. The short column of vapour traversed by the narrow beam in the high vacuum compartment gives off scattered resonance radiation, and we should expect this to record itself as a faint penumbra around the sharply defined image imprinted by the primary beam. No trace of any such penumbra was found, from which we can infer that the effect is negligibly small in comparison with that of the primary wave. This made me suspect that, even when the vapour is in a high vacuum, some true absorption of energy must take place, for it is obvious that the magnitude of the effect due to the resonance radiation will decrease in proportion to that of the primary wave as the factor of true absorption is introduced. It appeared possible to determine in this way, just what proportion of the energy diverted from the primary beam was absorbed and what proportion was scattered. I accordingly placed the quartz lens at the centre of the box, with the plate and absorption cell at the end opposite to that on which the perforated paper cone was fastened. This gave me a sharply focussed image of the circular aperture in the cone on the photographic plate, which was placed as before with the film in contact with the anterior quartz window. I now got a very intense beam of light from the resonance lamp, and a very black spot upon the plate with a distinct trace of a corona around it due to the scattered radiation (Pl. XII. fig. 10). Air was now admitted to the cell and the experiment repeated. No trace of the corona appeared as was to be expected, as is shown in Pl. XII. fig. 11.

This experiment will be better understood by reference to Pl. X. fig. 5, in which the scattered rays which produce the corona are represented by arrows. The question now is, how great an effect from these scattered rays are we to expect in comparison with the effect produced by the primary beam

after its passage through the cell? A rigorous calculation involves some difficulties, but we can make an approximate estimate in the following way. In the experiment as it was tried, the thickness of the cell was 10 mm., and the intensity of the primary beam was therefore reduced to one quarter of its original value, or in other words 75 per cent. of the energy was scattered, and 25 per cent. reached the plate as direct rays and recorded itself on a circular area 4 mm. in diameter. It is evident that the intensity of the scattered resonance radiation from the first layer of molecules encountered by the primary beam will be most intense, but its intensity will be reduced when it reaches the plate, by its passage through the gas, in the same proportion as is the intensity of the primary ray, which excites the last layer of molecules to a much feebler luminosity. The intensity of all of the layers as seen by the photographic plate would thus appear to be equal. It is now evident that the 75 per cent. of the energy diverted from the primary beam, since it is given out in all directions, is distributed over a complete sphere, and we shall probably go not very far wrong if we assume it all as coming from the first layer, which will make our sphere of radius equal to 10 mm. (the thickness of the cell), for in the actual experiment the photographic plate was placed in contact with the anterior window, and not at a distance as shown in the figure. The area of the sphere is 1256 mm. and the area illuminated by the primary beam 12 mm., the ratio of the areas being as 1 is to 105. We have then a radiation of intensity 3 distributed over area 105 (scattered), and radiation of intensity 1 concentrated on area 1. The direct image ought, therefore, to be about 35 times as bright as the corona. I made a rough measurement of this ratio and found it to be in the neighbourhood of 1:40, which agrees as well as we could expect, considering the way in which the calculation was made. The calculation was made on the assumption that no true absorption occurred, and the fact that there is some agreement between the calculated and the observed ratio indicates that we are dealing with pure scattering when the mercury vapour is in a high vacuum. The destruction of the corona by the admission of air is the direct consequence of the introduction of the factor of true absorption. I am of the opinion, however, that the ratio of the intensity of the secondary radiation to that of the primary, furnishes us with a better method of determining the ratio, and as I have already mentioned, the value obtained leads me to think that in a high vacuum there is no true absorption. A rigorous calculation of the ratio under specified conditions

is much to be desired, and could be easily tested by experiment. The calculation could be made for a beam of either rectangular or circular cross-section. I believe that a beam with a square cross-section will prove best, and it must be remembered that in the experiment we photograph the entire mass of the gas, as seen from the side. I found that with a beam of this description the intensity of the secondary radiation close to the beam of primary radiation was in some cases equal to one quarter of the value of the latter, though it fell off very rapidly in value as the distance from the primary beam was increased.

It thus appears that the destruction of the secondary resonance radiation is the result of the introduction of the factor of absorption, but it seemed best to test other hypotheses if possible. The only alternative that I have been able to think of is the possibility that the presence of the air alters the wave-length of the emitted light slightly so that it is no longer capable of exciting the vapour. The change necessary to accomplish this would be very slight, too small in all probability to be detected by any spectroscope except those of the highest resolving power. Another method, equally satisfactory and involving less difficulty than the use of a spectroscope, occurred to me. This we may call the method of the differential vacuum. A double cell with a quartz partition was constructed, of the form shown in Pl. X. fig. 6. Each compartment contained a drop of mercury, and the monochromatic light from the arc was focussed at the centre of the lower compartment, which was exhausted to a pressure of 6 mm., previous experiments having shown that the secondary radiation is practically unnoticeable at this pressure. The upper compartment was highly exhausted. The point at which the rays were focussed was brought as close as possible to the under side of the horizontal partition separating the two cells, and as close as possible to the window through which the radiation was photographed, to avoid the loss of light due to an intervening layer of vapour. If now there is a change of wave-length due to the air in the lower compartment, the light (emitted by the directly excited vapour) which passes up through the quartz partition will be unable to stimulate the vapour in the upper compartment. If, on the contrary, the absorption hypothesis is correct, the vapour in the upper compartment will glow, since we have eliminated absorption here by the complete removal of the air. The photograph showed the secondary radiation in the upper compartment, and the ratio of its intensity to that of the primary was about the same as

when both compartments were completely exhausted. This disposes of the second hypothesis, and is fully in accord with the absorption explanation.

*Transition from Irregular Scattering to Regular Reflexion
by the Molecular Resonators.*

I have already alluded to the selective reflexion of monochromatic light by very dense mercury vapour, which I made a study of some years ago, and the transition from diffuse scattering to this regular reflexion has been made the subject of experimental investigation. Regular reflexion can occur only when the resonators are so closely packed together that the primary wave is stopped completely by a layer the thickness of which is of the order of magnitude of the wavelength. If the resonators are so sparingly distributed in space that the incident wave penetrates to any appreciable depth, their radiations do not combine to form a reflected wave in the usual sense of the term. Planck, I think, has somewhere mentioned the circumstance that the radiations from the resonators destroy the primary wave on account of their lag in phase, but that those in the opposite direction, there being no primary wave travelling in this direction with which they interfere, give rise to a wave which constitutes selective reflexion. If this occurred, except in the special case in which the wave is stopped at the boundary, it would constitute what we might term "volume reflexion" as contrasted to surface reflexion, but the phenomenon has no existence, I feel sure. It seemed so easy, however, to get evidence of volume reflexion if it existed, that I made one experiment, rather with the idea of convincing myself of its non-existence than anything else. A cell was made of the form shown in Pl. X. fig. 7 and a divergent beam passed into it through the oblique quartz plate. If even a very small percentage of the energy emitted by the resonators was returned towards the source, *i. e.*, in the direction of the primary rays reversed, we should have a converging system of rays which would be in part reflected from the oblique quartz plate and come to a focus on the photographic plate P. The plate, however, showed only a uniform darkening due to the light irregularly scattered by the resonators.

We do, however, obtain regular reflexion when the density of the vapour is so great that the wave can penetrate only to a very small depth, and I next investigated the subject of the density at which the change from scattering to regular reflexion takes place. A quartz bulb containing

a drop of mercury, exhausted and sealed, was mounted just above a vertical chimney of sheet iron which served to immerse the bulb in the hot gases rising from a large Bunsen burner. A high temperature quartz thermometer was mounted with its bulb in contact with the quartz bulb, and by regulating the height of the flame of the burner, the bulb could be kept at any desired temperature. A divergent beam of the 2536 light was thrown upon the bulb by the quartz spectrograph, and the bulb photographed with the quartz camera. At room temperature the entire interior of the bulb was shown by the photograph to be filled with a uniform glow. As the temperature rose this glow was confined to the wall which received the direct rays from the spectrograph, owing to the failure of the radiation to penetrate to the interior. As the density of the vapour increased this glow appeared to draw in or close around the bright point which represented the image of the source reflected from the inner wall of the bulb. Two of these points usually appear in the picture, one reflected from the outer, the other from the inner wall. They are the virtual images of the source in the spherical mirror formed by the wall of the bulb. This contraction of the glow struck me as very peculiar, as it reminded one of the reflexion from a slightly corrugated surface, or a surface which has been very finely ground but not polished. I obtained it with the bulb and with a small flask. Pl. XI. figs. 5 and 6 show the phenomenon, the pressure of the mercury vapour being recorded on each photograph. I made a calculation by elementary methods of what was to be expected when the resonators became more closely crowded together, and came to the conclusion that such a drawing-in or contraction of the glow was not to be expected, but that what would actually occur would be a gradual diminution of the intensity of the glow, which at low pressures is spread uniformly over the illuminated wall, and a simultaneous increase in the intensity of the small image reflected from the inner wall. I now prepared a new bulb, which had never been heated or used in any experimental work, and found no trace of the contraction of the glow. A careful examination of the old bulb and the flask in a strong light revealed the presence of a slight amount of devitrification of the inner surface, the reflected image of the sun appearing surrounded with a fairly bright halo. This circumstance at once explained the contraction of the glow with increasing vapour pressure. As the density of the mercury vapour increased, the reflecting power of the inner wall increased, much as if a deposit

of a metal was being gradually thrown down upon it, and this increase of the reflecting power was sufficient to develop the diffraction halo due to the slight roughness of the inner wall. The fact that the contracting glow usually had a definite though irregular shape, and was frequently accompanied by neighbouring patches of lesser intensity, made me suspicious of the phenomenon in the beginning, but it was not until I noticed the slight devitrification of the surface that I was able to give a satisfactory explanation of the thing. In Pl. XI. fig. 6, the last impression was taken after the mercury arc had been burning for half a minute, and no longer emitted the exact frequency for which the mercury molecules responded. The reflexion in this case is due wholly to the quartz, and we see only the two minute points of light previously referred to.

The real phenomenon is shown in Pl. XI. fig. 7, made with the clean bulb. A and B were taken at room temperature, the former with a five-second exposure, the latter with one of half a second, to bring out better the relative intensities of the two images reflected from the inner and outer walls. I threw these out of focus a little, so that their relative intensities could be better determined. They appear expanded into circles of light due to zonal errors of the lens. It is clear that at room temperature the lower circle is much brighter than the upper, which was the one reflected from the inner wall. The other pair of circles are reflected from the back wall, and disappear in the other pictures owing to the failure of the radiation to penetrate to the back. Pictures C and D were made with a pressure of mercury vapour of about 20 mm. The glow is now confined to that portion of the wall which receives the direct rays, and the image formed by the outer wall is still brighter than that formed by the inner, the ratio being about the same. E and F were made with a pressure of very nearly one atmosphere. The diffuse glow has entirely disappeared, and there remain only the two regularly reflected images, the upper circle now being distinctly brighter than the lower. That this image (the upper circle) really came from the inner wall was proved in the following way. The heated bulb was cooled on the illuminated side by a blast of air. This caused a very fine "dew" of mercury globules to condense on the wall, practically silvering it on the inside. A photograph was immediately taken and the upper circle of light was found to be the brighter of the two, as was the case with the dense mercury vapour. The diffuse reflexion begins to

weaken at a pressure of about 2 cm. and is practically gone at 70 cm.

Polarization Experiments.

Inasmuch as I have discovered strong polarization in the fluorescent light emitted by sodium, potassium, and iodine vapour, I fully expected to find it in the case of the mercury resonance radiation, as the mechanism of the emission would appear to be much simpler in this case than in the other cases where we have, in addition to the resonance radiation, other associated frequencies emitted, which give rise to what I have named resonance spectra. No trace of any polarization could be detected with a Babinet compensator mounted in front of the resonance lamp. A small Foucault prism was used as an analyser, as ordinary Nicol's prisms are opaque to the ultra-violet on account of the Canada balsam with which they are cemented.

Experiments with the Resonance Lamp.

The radiation emitted from the exhausted quartz bulb is so homogeneous, that a layer of mercury vapour 5 mm. thick and at the pressure which it has at room temperature (0.001 mm.) reduces its intensity by about one half. Various investigations with the vapour at exceedingly low pressure at once became possible. It is as if we had a gas which appeared quite black even at pressures commonly employed in vacuum-tubes. It will be possible to study the rate at which the vapour diffuses into other gases at low pressures, and it may be possible to tell in this way whether the resonators are in reality mercury molecules or larger aggregates.

I made two photographs which illustrate what a sensitive detector of small traces of mercury vapour we have in the light of the resonance lamp. A quartz bulb having an internal diameter of 1.5 cm., containing a drop of mercury, was mounted in front of a photographic plate in a dark box and illuminated with the light of the lamp. The bulb cast a shadow as black as ink. The bulb was now opened, the mercury drop removed, and the bulb washed out with nitric acid and distilled water, heated nearly red-hot and a blast of air blown into it, and again photographed. It still gave the black shadow, though not as black as before. It was only by prolonged heating to a red-heat and much rinsing out with an air current that I was able to obtain a shadow picture which showed the flask transparent. The flask had been

previously heated until the mercury vapour in it had a pressure of several atmospheres, and I imagine that the inner surface may have adsorbed some of the vapour, which was not removed by the acid. A chemist would undoubtedly have called the flask clean, after the first treatment which I gave it. The two photographs are reproduced on Pl. XII. fig. 8.

I next drilled a shallow cavity in the end of a brass cylinder, warmed it to a temperature of perhaps ten degrees above the temperature of the room, and placed a drop of mercury in the cavity, the drop standing up above the level of the end of the cylinder. This was photographed in the dark box by the light of the lamp, and the picture showed the black column of mercury vapour carried up by the convection current of warm air (Pl. XII. fig. 9).

I am at present setting up a Michelson interferometer with a fluorite plate coated with a cathode deposit of gold for the purpose of ascertaining how large a difference of path is possible in the case of interference fringes formed by the light of this lamp. I imagine that the light may turn out to be more homogeneous than that of any other source with which we are acquainted. Of course it is possible that the line itself is complex, in which case matters will be different. The dispersion of the vapour in the vicinity of the 2536 line will also be investigated with the same apparatus. It will be interesting also to place the resonance lamp in a powerful magnetic field, and study the Zeeman effect for a gas radiating by resonance instead of under the action of an electrical or other stimulus.

It even appears possible that the electric analogy of the Zeeman effect can be detected with the resonating mercury vapour, since it can be brought to a high luminosity in a vacuum which is practically non-conducting, that is if the vapour does not become conducting when excited by the ultra-violet light, which I doubt; for a roughly carried out experiment with a small gold-leaf electroscope showed no conductivity when the vapour in the bulb between two electrodes was excited. We cannot infer from this what it would do with a potential sufficient to give say a 20 cm. spark in an alternating spark-gap, but I have a feeling that the vacuum would support it.

In fact a very wide field of investigation appears to be opened by the discovery of the very remarkable behaviour of the vapour of mercury at very low pressures.

This paper forms the third of a series upon the optical

properties of mercury vapour, the first being upon the fluorescence, etc. of the vapour (this journal, vol. xviii. p. 240), and the second, on the selective reflexion of monochromatic light by mercury vapour (*tom. cit.* p. 187). The investigation has been made possible through a grant from the Rumford fund of the American Academy of Arts and Sciences, and my thanks are due to the members of the Rumford committee for their generous aid.

LXVIII. *The Distribution of the Active Deposit of Radium in an Electric Field.* By E. M. WELLISCH, Assistant Professor of Physics in Yale College, and H. L. BRONSON, Professor of Physics in Dalhousie College, Halifax*.

1. Introductory.

THE present paper contains the results of a series of experiments which were carried out at the Sloane Physical Laboratory of Yale College, and which were undertaken with a view of throwing light on the mechanism involved in the transmission of the active deposit of radium to the electrodes in an electric field or to the exposed solid surfaces in the absence of such field. In order to account for this transport of activity one of us† had already suggested a theory in which the view was taken that the transmission was effected as a result of the interaction between the active deposit particles (or restatoms) and the ions formed in the gas by the radiation accompanying the radioactive disintegration; in particular, an attempt was made to explain on this theory the experimental result obtained by Rutherford‡ and Franck§ that the restatoms moved through the gas with the same velocity as the positive ions.

The original object proposed in the present experiment was to ascertain whether the distribution of activity on the electrodes could be affected in any way by the application of an extraneous source of ionization such, for instance, as that produced by causing intense Röntgen rays to pass through the gas.

We might be permitted to anticipate here the results of the present experimental investigation and to state that, although the application of such extraneous source of ionization has so far been found to produce little or no effect on

* Communicated by the Authors.

† Wellisch, *Verh. Deuts. Phys. Ges.* xiii. p. 159 (1911).

‡ Rutherford, *Phil. Mag.* ser. 6, v. p. 95 (1903).

§ Franck, *Verh. Deuts. Phys. Ges.* xi. p. 397 (1909).

the distribution of activity, nevertheless a decided interaction has been found to take place between the restatoms and the ions produced by the radiations which accompany the formation of these particles.

The results of previous experimenters with regard to the distribution of the active deposit under various conditions have shown a lack of agreement which in our present experiments has been traced to the fact that the potentials employed were often far from sufficient to saturate even approximately the radioactive ions.

2. Experimental Procedure.

The radium emanation used in our experiments was obtained from two sources, for the use of both of which we are indebted to the kindness of Prof. Boltwood. One source consisted of a solution of radium salt contained in a glass vessel so constructed as to permit vigorous bubbling when a current of gas was passed through it; the other source was a quantity of carnotite contained in a glass jar, which was adjusted to permit of rapid connexion to the testing vessel.

The emanation was in most cases passed through glass-wool and phosphorus pentoxide before entering the test vessel; no effect on the distribution was observed, however, by omitting these precautions.

Different forms of test vessels were employed; the vessel which was used practically throughout and to which all our experiments apply, unless mention is made to the contrary, consisted of a brass cylinder with an aluminium bottom and a brass central electrode sprung into a stout brass holder so as to permit of rapid detachment. The vessel was provided with a guard tube which was connected to earth; this guard tube was slightly tapered so as to make a good fit with the ebonite plug which supported the central electrode. Stop-cock grease was employed to ensure complete tightness.

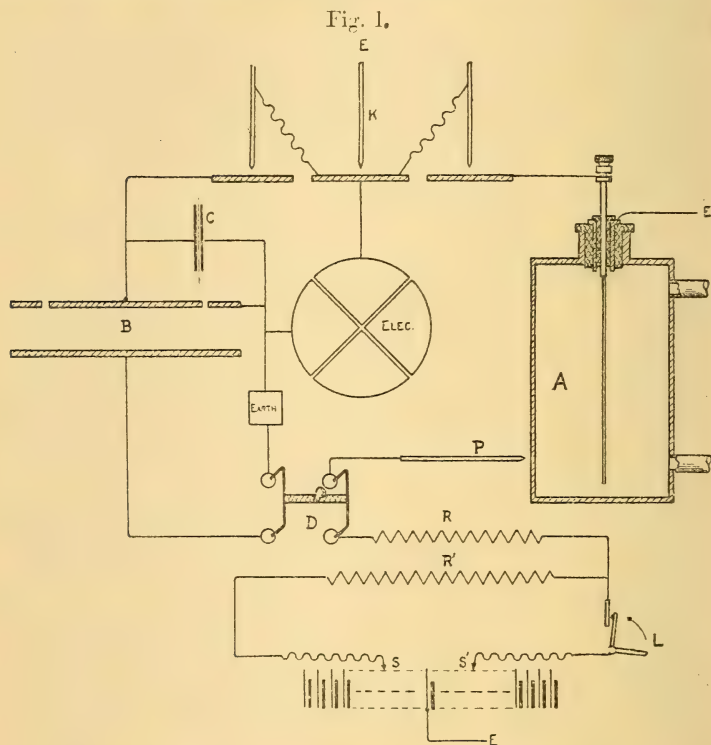
The dimensions of this vessel were as follows:—

Height of containing portion	140	mm.
Inner diameter	58	„
Exposed length of central electrode .	101	„
Diameter of central electrode	1.83	„

The measurements of the activity of the central electrode were made in a vessel identical to the above except that as mentioned below no ebonite and in consequence no guard tube was employed.

The diagram of connexions and the disposition of apparatus

are given in fig. 1. The test-vessel A was supported by brass clips mounted on ebonite; these clips were connected



to the battery through carbon resistances R , R' , the changes of potential being effected by means of the adjustable contacts s , s' , and the key L . B represents a parallel plate vessel which was employed in order to communicate definite induced charges to the electrometer system whenever occasion arose. C is a capacity consisting of two thin sheets of tinfoil separated by a thin sheet of mica; this capacity, together with that of B , could be added to the system by means of the key K , and the total capacity of the system was then increased $21\frac{1}{2}$ times. The electrometer was of the Dolezalek pattern with a platinum suspension. The needle was charged to a potential of 120 volts, and with this potential the sensitiveness was 180 mm. per volt on a scale about 1 metre distant.

The Röntgen-ray bulb, which was enclosed in a lead-covered box and which was employed whenever it was

desired to increase the ionization current in the test-vessel, is not shown in the diagram; the rays were admitted through an aperture in the lead directly beneath the aluminium bottom of the vessel.

For potentials up to 1200 volts a battery of small accumulators was employed. For the larger potentials a Wimshurst machine was used which was driven by an electric motor; it was found that the voltage obtained by this means was surprisingly steady, although the slight variations were sufficient to prevent any accurate measurements of the ionization current through the gas. The voltage was regulated by means of an adjustable spark-gap, and was measured with a Braun electrometer.

The method of procedure was in general as follows: after the introduction of the emanation the vessel was allowed to remain in position under the desired conditions of potential, pressure, &c., for a period sufficiently long to enable the emanation and the resulting activity to get into equilibrium. This period was usually about three hours, and was never less than $1\frac{1}{2}$ hours; readings of the ionization current were taken at intervals so as to note the growth of activity and the establishment of equilibrium. The emanation was blown out by means of a strong current of air from a force-pump; the ebonite plug containing the central electrode was then removed, care being taken that this electrode did not touch the case.

The activity on the case was measured by observing the ionization current to which it gave rise; for this purpose a fresh electrode was suspended in the vessel by means of the brass holder shown in the diagram; by thus avoiding the use of ebonite the activity could be measured with great precision. This procedure was rendered necessary because, as is subsequently shown, an accurate determination of the activity on the case was the most important factor in the experiments. It was found that handling ebonite insulation, even with great precaution, resulted in the production of disturbing electrical effects which were sufficient to render uncertain the subsequent measurements. The activity at any time after the removal of the emanation was then measured by observing the electrometer rate.

In order to determine the activity on the central electrode this electrode was removed from its holder by means of a pin, which passed through a small hole, and was then suspended in the second vessel in the same manner as described above; the electrometer rate could then be taken at any definite time dating from the removal of the emanation.

In practice it was found convenient to measure the case activity at 10, 15, and 20 minutes, and the central electrode activity at 25, 30, and 35 minutes after the emanation had been removed; the maximum activity, *i. e.* the activity when in equilibrium with the emanation, was then calculated by means of the figures given by one of us * for the rate of decay of the activity resulting from a long exposure. The consistency of this calculated maximum determined the number of readings necessary for the measurement of the activity, but usually those just mentioned amply sufficed.

In practically all our experiments the activities were measured by observing the ionization currents to which they gave rise in air under the ordinary conditions when a potential of +160 volts was applied to the vessel employed. Although this potential was not sufficient to saturate the currents, subsequent experiments showed that the ratio of the two activities as thus measured was not altered by using a larger voltage.

A typical set of readings is given later.

3. *Experiments with Small Applied Potentials.*

It is well known that for moderately high potentials the activity is concentrated to a very large extent on the negative electrode in an electric field; Schmidt† has shown that when small potentials are employed the cathode activity decreases in a manner analogous to the diminution in electric current which follows as a result of recombination of ions; in fact, he came to the conclusion that the active deposit particles behave in a manner similar to the positive ions. The first set of experiments tried in the present series had as object to find whether the amount of activity that was deposited on the cathode when a small positive potential was applied to the case could be altered when the ionization in the gas was so increased by means of Röntgen rays that the electric current through the gas was at least as great as if a large potential had been applied without any extraneous source of ionization.

In this set of experiments the rods were exposed as cathodes to the process of activation for a period of 10 minutes, both with and without the application of Röntgen rays, the testing vessel containing air at 1 atmosphere; the activities were measured at various intervals after removal, and were then directly compared. Preliminary trials which were

* Bronson, *Phil. Mag.* ser. 6, xii. p. 73 (1906). In order to calculate the maximum activity from the rates determined at the times given above, the observed rates have to be multiplied by the factors 2.02, 2.25, 2.41, 2.58, 2.75, and 2.96 respectively.

† Schmidt, *Phys. Zeits.* ix. p. 184 (1908).

made showed that in the process of removing one rod and substituting another less than 2 per cent. of the emanation escaped.

A result of one set of measurements is given below :—

With +4 volts on case and 10 minutes exposure, activity of cathode 10 minutes after removal is represented by an electrometer rate of 1.1 mm. per sec.

With same applied potential and strong Röntgen rays passing through the vessel during the whole time of exposure the corresponding rate was .88.

As a rough idea of the relative currents involved the following figures are given; in these instances the rates were determined with the extra capacity added to the system.

Ionization current immediately after introduction of emanation and with +160 volts on case: 3.3 mm. per sec.;

with 4 volts rate was 1.05;

with 4 volts and Röntgen rays rate was 5.21.

In the last two instances there was, of course, a deposit of activity on the walls of the vessel.

Other experiments were made with the same object, in some instances large amounts of activity being previously concentrated on the walls of the vessel so as to increase still further the ionization. The results were of the same nature, viz. to show a small decrease in the amount of activity deposited on the cathode when additional ionization was produced; the decrease could be accounted for if we adopt the view that the restatoms behave as positive ions, and are subject to increased recombination with the negative ions produced by the application of the extraneous radiation.

4. *Experiments with Larger Potentials. Air at 1 atmosphere.*

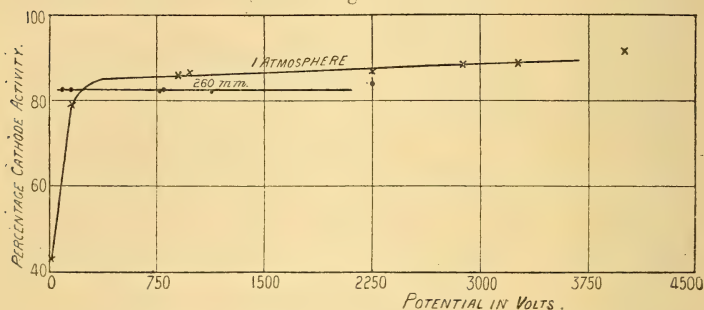
Experiments were next made to ascertain the percentage of the total activity that was deposited on the cathode when larger positive potentials were applied to the case. The result of this set of measurements is given below (Table I.),

TABLE I.—Emanation in Air at 1 atmosphere.

Potential in volts.	Percentage cathode activity.
18	42.7
160	79.1
900	85.9
975	86.6
2250	86.9
2800	88.5
3250	89.0
4000	91.3

and is exhibited as a curve in fig. 2, which refers to air at 1 atmosphere; the method of procedure for determining the points has already been given in section 2.

Fig. 2.



It will be seen from an inspection of this curve that the percentage cathode activity always increased with the applied potential, a result which indicates that there are practically no negative carriers of activity; all the so-called anode activity to which reference is made by many investigators is due to the diffusion to the walls of the vessel of uncharged restatoms. A slight correction has on this account to be made for the amount of uncharged activity that diffuses to the cathode during the exposure; this correction was made by estimating the relative areas of the exposed surfaces of cathode and case, which were found to be in the ratio 1 : 50, and assuming that the uncharged restatoms were distributed in this proportion. The true percentage cathode activity, that is, the number of positive carriers expressed as a percentage of the total number of carriers, is obtained from the percentage cathode activity (p), as determined experimentally, by evaluating the expression $\frac{51p}{50} - 2$. All values given in this paper for the percentage cathode activity denote the true percentage obtained by correcting in this manner.

A typical set of measurements is given below:—

Emanation passed through P_2O_5 and glass-wool into vessel containing air at 1 atmosphere. +975 volts on case. Exposure about 2 hours.

Equilibrium rate with added capacity: 6.17.

Activity on case measured at 10 and 15 minutes after removal of emanation; rates with added capacity: .19 and .17 respectively.

Activity on cathode measured at 20 and 25 minutes after removal of emanation; rates with added capacity: 1.05 and .98 respectively.

Calculated maximum activity on case: '38.

Ditto cathode: 2·53.

Ratio of max. cathode to max. case activity: 6·66 : 1.

Percentage cathode activity: 86·9.

True percentage cathode activity as corrected for diffusion of uncharged carriers to cathode: 86·6.

It is difficult to estimate with precision the experimental error in the determination of the percentage cathode activity. A slight error probably arises from the fact that the cathode and case activities are determined by means of ionization which is differently distributed. This has been shown experimentally to have a negligible effect on the relative values of the percentage cathode activities for different potentials, the determination of which was really the object of the experiment. As mentioned above, it was important to make an accurate determination of the maximum activity on the case. An error in the determination of this activity leads to approximately the same percentage error in the determination of the percentage cathode activity; this error in all our experiments is probably less than 2 per cent.

The plotting of a curve such as that of fig. 2 is obviously only possible if the percentage cathode activity is independent of the amount of emanation used in the experiment. This fact was demonstrated repeatedly during the course of our investigations; as an instance of the wide range over which this holds it may be mentioned that the percentage cathode activity was the same with 900 volts on the case when the amounts of emanation in the vessel were such as to afford equilibrium rates of 5·32 without any added capacity and 16·1 with the added capacity, *i. e.* rates which are roughly in the ratio 1 : 65. When we are working in the earlier part of the curve, *i. e.* with relatively small potentials, this independence no longer holds good; but for the higher potentials the effect of the amount of emanation within a large range becomes negligible.

The curve bears a striking resemblance to the curves which have been experimentally determined for ionization by α particles. Many observers have drawn attention to the "lack of saturation" which is a marked feature of such curves; in particular, this phenomenon has been the subject of special investigation by Bragg*, Kleeman†, Moulin‡, and Wheelock§. Reference is made to this point later (section 7).

* Bragg, *Phil. Mag.* ser. 6, xi. p. 466 (1906).

† Kleeman, *Phil. Mag.* ser. 6, xii. p. 273 (1906).

‡ Moulin, *Compt. Rend.* cxlviii. p. 1757 (1909); *Le Radium*, vii. p. 350 (1910).

§ Wheelock, *Am. J. Sc.* xxx. p. 233 (1910).

The similarity was so striking as to suggest a more detailed study of the ionization curves for emanation in equilibrium and with different applied potentials.

It was found that within the limits of error the ratio of the two ionization currents obtained for two potentials not too low* was, like the percentage cathode activity, independent of the amount of emanation in the vessel; and, moreover, that this ratio was identical with the ratio of the percentage cathode activities corresponding to these two potentials.

As an example of the results obtained in this connexion it will suffice to compare the ratio 1.09 of the percentage cathode activities obtained with potentials 975 and 160 volts respectively with the corresponding ionization currents. From our values for the ionization currents in air at 1 atmosphere pressure obtained in three experiments when widely different quantities of emanation were employed, we deduce the following figures:—

Ratio of current with V volts to that with 160 volts:

= 1.10 when $V = 875$,

= 1.10 when $V = 980$,

= 1.07 when $V = 900$.

It would serve no useful purpose to reproduce in full any of the ionization curves because, in the first instance, the early slope of the curve depends markedly on the amount of emanation employed, and, secondly, because the comparison could only be made over the limited range from about 100 to 1000 volts, as the ionization current could not be accurately measured when the larger potentials were employed.

That the equality of the ionization and activity ratios still holds approximately at low voltages when a constant amount of emanation was employed was verified by measuring the percentage cathode activity with 18 volts applied, and the ionization currents for 18 volts and higher potentials, it being known that the percentage cathode activity at the higher potentials was independent of the amount of emanation in the vessel. The following results were obtained:—

Percentage cathode activity with 18 volts: 42.7.

Ditto 160 volts: 79.1.

Ratio: .54.

Ionization current with 18 volts: 6.6.

Ditto 160 volts: 11.4.

Ratio: .58.

* The potentials should be sufficiently large to prevent volume recombination as distinguished from columnar recombination, *i. e.* should be sufficient to saturate a uniform distribution of Röntgen ray ions equal in number to those produced by the α radiation.

The agreement is only rough, and further experiments will be necessary at these small potentials.

The percentage cathode activity increases so slowly with the higher potentials applied that it appeared as if some definite fraction of the activity was always bound to be deposited on the case. Subsequent experiments made with large potentials obtained by using the Wimshurst machine showed, however, that the percentage cathode activity continually increased with the potential. It is not out of place to mention briefly here two sets of experiments which were conducted prior to the use of the Wimshurst machine.

It was suggested that, if a large uniform electric field were applied, possibly the number of uncharged carriers might become insignificant. For this purpose the emanation was introduced into a vessel consisting of two parallel electrodes of aluminium (each 58 mm. in diameter) insulated by an ebonite ring 20 mm. thick; the vessel contained air at a pressure of 1 atmosphere. Experiments made with applied potentials of 160 and 1000 volts gave values of 75 and 82.6 respectively for the percentage of positively charged carriers.

The second set of experiments had as object to determine whether RaA was deposited on the case. To test this point the cylindrical vessels were employed as usual and large potentials applied, but exposures of only 1 minute duration were made. It was found that the resulting curve of decay of the case activity had the characteristic properties of the curves of decay for the activity due to a short exposure to the radium emanation.

Mention might also be briefly made here of some experiments which were performed to ascertain whether there was any alteration in value of the percentage cathode activity resulting from a long exposure with large positive potentials applied to the case when throughout the exposure the ionization current was greatly increased by the passage of Röntgen rays through the vessel. The alteration, if any, was very small and for the present, at any rate, we must assume that the action of the Röntgen rays is without effect on the distribution of the activity.

5. Experiments with Air at Reduced Pressure.

The experimental results described in the preceding section strongly suggest that over a wide range of potentials the percentage of the total activity which is deposited on the case represents the percentage lack of saturation of the positive ionization current. These experiments related to the activity distribution in air at a pressure of 1 atmosphere. Now

Moulin and Wheelock have shown (*loc. cit.*) that the ionization produced by α particles is more readily saturated when the pressure of the gas is reduced; it was, therefore, of interest to determine whether the percentage cathode activity would follow the positive ionization current when the gas pressure was reduced. For this purpose the emanation was introduced into the testing vessel, which contained air at a pressure of 260 mm., and the percentage cathode activity was determined for various applied positive potentials. The results are given below (Table II.), and are exhibited as a curve in fig. 2.

TABLE II.

Emanation in air at a pressure of 260 mm.

Potential in volts.	Percentage cathode activity.
80	82.5
150	82.5
775	81.8
790	82.2
1130	81.8
2250	83.8
2250	84.2

It is noticeable that although the percentage cathode activity for 150 volts is greater than the corresponding value for a pressure of 1 atmosphere, nevertheless when the higher potentials are reached the values are smaller at the lower pressure.

When the ionization due to the emanation in equilibrium with its activity and in air at a pressure of 260 mm. was measured for various applied positive potentials, it was observed that the alteration of ionization with potential was so extremely slow as to suggest saturation. Over the range for which the ionization could be measured this alteration was too small to justify comparison with the figures given for the percentage cathode activity; the striking feature is that both curves approach more nearly to the horizontal than the corresponding curves for a pressure of 1 atmosphere. The figures for the lower pressure show that for large potentials the activity is farther from saturation than at 1 atmosphere; it is therefore only reasonable to conclude that in the case of ionization the percentage lack of saturation is greater at the lower than at the higher pressure.

The figures given in Table II., although sufficiently consistent to justify the conclusion just given, nevertheless exhibit slight irregularities which are being made the subject of further investigation. In the first instance the values for the percentage cathode activity for potentials in the neighbourhood of 1000 volts show a slight falling off as compared with those corresponding to the smaller potentials. The explanation of this effect appears to lie in a distortion of the field in the neighbourhood of the ebonite plug, arising from some action of the α radiation on the ebonite; this distortion would result in some of the cathode activity being deposited on the plug instead of on the central electrode. Corresponding difficulties arose for the ionization measurements at the reduced pressures.

The increase of the percentage cathode activity in the neighbourhood of 2000 volts is probably real, although the number of experiments in this connexion is not yet sufficient to justify any definite statement. It is, however, of interest to record that throughout the exposure with these high potentials a large current due to ionization by collision was passing through the gas.

Finally, it might here be mentioned that a complete set of observations for the distribution of the activity with various applied potentials, both for air at 1 atmosphere and for air at a pressure of 250 mm., had previously been made, using the same test-vessel, but with the guard-tube projecting a short distance into the volume of the gas. By reason of this some of the activity which belonged properly to the cathode was measured as "case activity," so that the resulting values for the percentage cathode activity were too small. The curves obtained both for activity and ionization exhibited the same general features as those previously described. Some of the results obtained are given below; these figures are not comparable with those given above, which were all obtained after the guard-tube had been cut down.

Emanation in Air at 1 atmosphere.

Potential in volts.	Percentage cathode activity.
160	76.2
880	84.1
2750	86.2

726 Profs. Wellisch and Bronson on the *Distribution of*
Emanation in Air at 250 mm. pressure.

Potential in volts.	Percentage cathode activity.
160	81.2
920	81.9
2500	82.1

6. *Experiments with Air at Pressures greater than*
1 atmosphere.

Several experiments were performed to ascertain the distribution of activity when the air in the testing vessel was at a pressure greater than 1 atmosphere. The results are given in Table III.; they were obtained in the early stages of the research when little information was at hand concerning the distribution of the activity for various potentials. For this reason the experiments appear very unsystematic; however, the results will serve to convey a good idea of the difficulty of obtaining approximate saturation of the activity, even with large applied potentials.

TABLE III.

Pressure, atm.	Potential in volts.	Percentage cathode activity.
1.6	+700	68.8
2.0	650	64.1
2.5	160	55.2
2.5	750	60.1
3.13	880	57.5
3.33	3750	80.6
3.53	750	53.8

The difficulty of saturating the ionization current through the gas likewise made itself manifest at these pressures; as an example it may be mentioned that with an applied potential of 1100 volts the ionization current due to a constant source of radiation increased as the pressure was increased from 1 to $2\frac{1}{2}$ atmospheres, and then continually decreased with any further increase in the pressure.

These considerations afford an explanation for the maximum of cathode activity which has been found by several experimenters to set in at certain pressures when a constant potential is employed.

No indication of any decided effect upon the distribution of the activity was obtained by subjecting the gas throughout the exposure to the influence of a strong source of Röntgen rays. In this experiment the vessel contained emanation in air at a pressure of $3\frac{1}{3}$ atmospheres; the applied positive potential was 1100 volts; the equilibrium rate with the added capacity was 5 mm. per sec., and with the Röntgen rays acting was 25 mm. per sec. The percentage cathode activity was 56.2, which is of the order that might have been expected from the previous results.

7. Discussion of Experimental Results.

In the interpretation of the experimental results which have been obtained in connexion with the distribution of activity the question arises immediately: what is the reason for the difficulty in saturating the cathode activity? Even under the most favourable conditions which have been employed in our work there is still about 10 per cent. of the activity deposited on the walls of the testing vessel. In an attempt to answer this question we are at once led to the corresponding problem in connexion with the ionization current which passes through the gas during the activation of the electrodes. Mention has already been made of the researches of Bragg, Kleeman, Moulin, and Wheelock in connexion with this aspect of the problem. Bragg explained the difficulty of saturating the ionization due to α particles by introducing the conception of initial recombination; viz. that the electron which is expelled in the process of ionization returns in a number of cases to its parent atom, and exceptionally strong electric fields are needed to exercise any appreciable preventive effect upon this tendency to recombine. Kleeman extended the experimental work, using Bragg's theory as a basis. Moulin ascribed the difficulty of obtaining saturation to the fact that the α particle ionized in columns, so that the density of ionization is not uniform throughout the gas when sufficiently small volumes of gas are considered. This localization of the ions would naturally result in a recombination more intense than that which would correspond to a uniform distribution in the usual acceptance of the term. Moulin showed that saturation appeared to be most difficult when the columns were parallel to the lines of force of the electric field; when, however, the α particles moved across the lines the ionization tended more readily to saturation. Wheelock continued the work, adopting the idea of columnar ionization; in particular, he showed that when the pressure

was reduced to about one third of an atmosphere saturation set in fairly readily. There can be little doubt as to the reality of this columnar effect and the intense recombination resulting from the local distribution of the ions; this is clearly brought out by the slowness with which the ionization current increases with the potential in the early stage of any curve for α particle ionization. The experimental results obtained in the present research appear to lead to a radically different explanation of the shape of the ionization curves at the higher potentials. It has been shown that for potentials which are not too low the ratio of the percentage cathode activities for two different potentials is equal to the ratio of the corresponding ionization currents due to the α particles, and over a wide range is independent of the amount of emanation employed, that is, of the intensity of the intrinsic ionization. This experimental result has already led to the suggestion that the fraction of the total activity which is deposited on the walls of the testing vessel is a measure of the lack of saturation of the ionization current, so that in general the percentage case activity is equal to the percentage lack of saturation of the current. The values given in section 5 for the percentage cathode activities at a pressure of 260 mm. are smaller for the higher potentials than the corresponding values for atmospheric pressure; we are consequently constrained to regard the percentage lack of saturation as being greater for the ionization currents at the lower pressure than at the higher pressure. The horizontality of the curves would thus appear to furnish no evidence as to the degree of saturation. The curves both for activity and ionization current do not appear to have horizontal asymptotes such as belong to the ordinary saturation curves for Röntgen-ray ionization. We must rather look upon the curves as having a continued upward slope, even when we are considering the ionization curves corresponding to low pressures. This upward slope suggests that extra ionization is produced by the electric field after the α particle has ceased to ionize.

On this view there must be present in the gas certain molecules, or neutrons, which are in a condition allowing of relatively easy ionization. It is highly probable that the molecules have already been put in this unstable condition by the action of the α particle; we may look upon this condition as the result of ineffectual attempts by the α particle at ionization, possibly as the result of actual ionization immediately succeeded by initial recombination. However, these molecules are left by the α particle in an electrically

neutral although unstable condition, and a certain number of them are afterwards resolved into ions, probably as a result of collision with the ions already established in the columns.

These neutrons are in all probability formed most numerous during the early part of the range of the α particle, when it is moving with its largest velocity. The approximately horizontal parts of the ionization curves such as are obtained at low pressures, or when the α particle moves perpendicularly to the lines of electric force, would therefore only represent saturation in the sense that all the free ions have been brought over to the electrodes because in these cases it is unlikely that an appreciable number of neutrons would be resolved into ions.

As far as the active deposit particles are concerned we may regard them as neutral restatoms which have been exposed to the action of the α particle at the moment of disintegration of the emanation atom; we would thus expect them to be for the most part radioactive neutrons which have in general to be subjected to further influence before acquiring a positive charge.

Experiments which are now in progress suggest also that the shape of the Bragg-Kleeman ionization curve can be accounted for by the formation of neutrons and ions in different proportions along the entire range of the α particle.

8. *Summary.*

(1) The distribution in an electric field of the activity resulting from a long exposure to the emanation of radium has been determined for various conditions of pressure, potential, &c.

(2) There appear to be no negatively charged carriers, all the so-called anode activity being due to the diffusion of uncharged carriers.

(3) The effect on the distribution obtained by causing Röntgen rays to pass through the gas during the exposure has been investigated; this effect was appreciable only when the activity and ionization were far from saturation.

(4) The difficulty of obtaining saturation both for the cathode activity and for the α ray ionization currents has been explained as being due to the formation by the α particle of neutrons, some of which are subsequently resolved into ions, probably by collision with ions already established in the columns.

LXIX. *Absorption Spectra and the Solvate Theory of Solution.* By HARRY C. JONES*.

[These investigations on the Absorption Spectra of Solutions were carried out with the aid of Grants from the Carnegie Institution of Washington.]

A DOZEN † or more independent lines of evidence have been discovered, all pointing to the conclusion that dissolved substances combine with more or less of the solvent. In a word, in dealing with solutions we must take into account not only the dissociation of the dissolved substance, but also its solvation, or power to combine with the solvent.

With this idea in mind it seemed highly desirable to study the absorption spectra of solutions. The absorption of light by dissolved substances is a resonance phenomenon; those wave-lengths that are absorbed finding something in the solution which they can throw into resonance with themselves. If the dissolved substance combines with more or less of the solvent, it seems reasonable to suppose that the substance would show different resonance from that which it would manifest in the uncombined condition. This conclusion is independent of whether the absorption of light by a dissolved substance is due to molecules, ions, or electrons.

It seemed that some knowledge might be gained in individual cases as to whether there was solvation, and if so, what was its order of magnitude, by studying the power of solutions to absorb light under changing conditions of dilution, temperature, &c.

This was, in general, the thought that led us to take up, six years ago, the problem of the absorption spectra of solutions in as broad a way as possible; and the work has been in progress continuously since that time, under Grants generously awarded by the Carnegie Institution of Washington. We have had at our disposal in this work Rowland concave gratings ruled by Dr. Anderson, which gave us the large dispersion necessary to separate properly the absorption lines and bands.

The absorption spectra of somewhat more than 6000 solutions have been photographed, and some conclusions reached whose bearing on the solvate theory are of interest and we hope of some importance.

For details concerning the methods of work and the

* Communicated by the Author.

† *Zeitschr. phys. Chem.* lxxiv. p. 325 (1910); *Amer. Chem. Journ.* xli. p. 56 (1909).

apparatus used, reference must be made to the earlier publications * of some of the results of this work. It should be stated that the grating spectroscope alone has been used.

The work begun by Jones and Uhler† had to do with three problems. They studied the effect on absorption spectra: of changing the concentration of the solution, of the addition of a dehydrating agent in the form of a second salt, and of the addition of water to non-aqueous solutions of the salt in question.

The results of this work were all interpretable in terms of the solvate theory of solution, and in terms of no other generalization; but it could not be said that any *direct evidence* for the theory was furnished by this earlier work.

The investigation which followed, however, furnished very direct evidence for the solvate theory. Jones and Anderson‡ studied the absorption spectra of about 1200 solutions; including salts of cobalt, nickel, copper, iron, chromium, neodymium, praseodymium, and erbium in water and the alcohols as solvents. They varied in some cases the total number of ions in the path of the beam of light; in other cases the number of ions was kept constant and the number of molecules in the path of the light was varied. This was all accomplished by changing the concentration of the solutions and suitably changing the depth of the solution through which the light passed. By keeping everything constant except some one of these factors, and observing the effect on the various lines and bands when a given one of these quantities was varied, it was possible to determine what produced a number of the lines and bands.

Thus, the ultra-violet absorption of cobalt salts was shown to be due to undissociated molecules or something contained within them, while the green cobalt band was produced by the cobalt atom or something contained within it.

The absorption spectra of solutions of nickel salts were due chiefly to the nickel atom; and, similarly, the absorption of copper salts in the red end of the spectrum.

The λ 3300 band of cobalt disappeared quickly with increase in dilution, even when the total number of molecules in the path of the beam of light was kept constant. It became more intense with rise in temperature. This band, obviously, could not be produced by ions, molecules, or atoms,

* Carnegie Institution of Washington, Publications nos. 60, 110, 130, and 160. Amer. Chem. Journ. xxxvii. p. 126 (1907); xli. pp. 163, 276 (1909); xliii. pp. 37, 97 (1910).

† Ibid. xxxvii. p. 126 (1907). Phil. Mag. xix. p. 566 (1910).

‡ Carnegie Institution of Washington, Publication no. 110.

but might be produced by simple hydrates formed by the breaking down of more complex hydrates with rise in temperature.

Cobalt salts show marked absorption in the red, only when very concentrated, at elevated temperatures, or in the presence of a dehydrating agent. The absence of red absorption at moderate concentration shows that this absorption is not due to ions. The conditions for the absorption in the red suggest that it might be due to molecular aggregates. This, however, is debarred by the fact that the red absorption increases with rise in temperature, while this would break down any such aggregates. We would, then, most naturally conclude that the absorption in the red was due to simple hydrates, since the conditions favouring this absorption favour the existence of such hydrates.

In a similar manner it was shown that the ultra-violet absorption of copper salts was connected with the solvation of the molecules—the absorption being smaller the more complex the solvate.

Direct spectroscopic evidence for the existence of solvates was furnished by Jones and Anderson in their study of salts of neodymium. A salt like neodymium chloride was found to have a very different absorption spectrum in water from what it had in methyl alcohol. Neodymium chloride in the proper mixture of water and methyl alcohol shows both the "water" bands and the "alcohol" bands. By varying the amounts of the solvents relative to one another, the relative intensities of the two sets of bands can be changed at will.

Neodymium nitrate in a mixture of water and methyl alcohol shows bands of the same character in the two solvents as the chloride.

Praseodymium chloride in a mixture of water and methyl alcohol shows the same kind of change as neodymium chloride. In this case an entirely new band appears in the alcohol, which has no analogue in the aqueous solution.

The existence of "water" bands and "alcohol" bands in the aqueous and alcoholic solutions, respectively, is interpreted by Jones and Anderson as direct evidence for the existence of hydrates in the aqueous solutions, and alcoholates in the alcohol solutions—in a word, is direct spectroscopic evidence for the solvate theory.

The largest amount and most direct spectroscopic evidence for the solvate theory of solution has been brought to light by the work of Jones and Strong, which has been in progress continuously during the past three years, and the results are

as yet largely unpublished in any scientific journal*. A careful study was made of the absorption spectra of cobalt salts in different solvents as affected by temperature. Glycerol solutions of these salts showed a different spectrum from aqueous solutions, indicating the presence of glycerolates in such solutions, as we have hydrates in aqueous solutions.

The effect of rise in temperature is to increase enormously the absorption of concentrated aqueous solutions of cobalt chloride, especially in the red. It is well known that such solutions turn blue on heating. The more concentrated the solution the lower the temperature at which this colour change takes place. There is a large amount of evidence which points to the conclusion that the change in absorption is due to a breaking down of the more complex hydrates with rise in temperature. If this is the true explanation of the phenomenon, the presence of a dehydrating agent such as calcium chloride or aluminium chloride ought to cause this change in absorption to take place at a lower temperature, since the dehydrating agent would assist the rise in temperature in breaking down the complex hydrates.

The results here are in accord with prediction. The addition of either of the above chlorides causes the great absorption in the red to take place in more dilute solutions at the same temperature, or in a given solution at a lower temperature.

It was further found that the temperature at which this marked change in the red absorption takes place is higher for aqueous and glycerol solutions than for solutions in other solvents; showing that the "hydrates" and "glycerolates" are more stable with respect to temperature than other solvates.

The effect of rise in temperature on salts of chromium was also studied, and was shown to be similar to the effect of rise in temperature on cobalt salts—the higher the temperature the greater the absorption.

The action of dehydrating agents on chromium salts was similar to that on salts of cobalt.

Absorption Spectra of Uranium Salts.

A fairly comprehensive study was made of the absorption spectra of uranium salts, to see especially whether there was evidence obtainable for the existence of definite solvate bands in different solvents. We studied both uranyl and uranous compounds.

* See Carnegie Institution of Washington, Publications 130 and 160.

It was soon found that an aqueous solution of uranyl chloride shows absorption bands in different positions from those of solutions in methyl alcohol. These differences were sufficiently great to merit careful study.

What these differences are can be best seen by giving the wave-lengths of a few bands in the different solvents.

Uranyl Chloride.

In water.....	λλ4025,	4170,	4315,	4460,	4560,	4740,	and 4920
In methyl alcohol...	λλ4090,	4220,	4345,	4465,	4590,	4760,	and 4930
In ethyl alcohol ...	λλ4100,	4250,		4400,	4580,	4750,	and 4900
In propyl alcohol ...	λλ4100,	4230,		4400,	4580,	4750,	and 4910
In isopropyl alcohol	λλ4100,	4250,		4360,	4560,	4750	
In butyl alcohol ...	λλ4100,	4240,		4390,	4560,	4750,	and 4970
In isobutyl alcohol .	λλ			4400,	4560,	4720,	and 4900
In ether	λλ4040,	4160,		4300,	4444,		and 4630
In methyl ester.....	λλ4030,	4160,	4280,	4440,	4620,	4790,	and 4920
In glycerol.....	λλ4025,	4140,	4260,	4400,	4540,	4720,	and 5050
In formamide	λλ			4450,	4650,		and 4840

The absorption spectra of uranyl nitrate in mixtures of water and methyl alcohol were photographed. The absorption in pure methyl alcohol was much greater than in pure water. As water was added to the alcoholic solution the absorption became less and less. In the mixed solvents the bands became very broad. A careful study of the structure of these broad bands showed that they were the "water" and "alcohol" bands coexisting; and not one set of bands shifted in position, and this, as we shall see, is an important point.

A simple method of reducing uranyl to uranous salts in solution was found to be the action of nascent hydrogen. This was obtained by introducing into the aqueous solution of the uranyl salt a bar of zinc, and then adding the acid of the salt in question. In this way uranous salts could be prepared, and several of them were found to have sufficient stability for our purpose. Uranous chloride, uranous bromide, and uranous acetate were thus made and their absorption spectra photographed and studied. These salts proved to be very useful for the detection of "solvent" bands, or the effect of the solvent on the absorption spectra of salts dissolved in it. The uranous bands are numerous, and what is far more important for our work, they are well defined with comparatively sharp edges, and their wave-lengths can be accurately determined. In this respect they are second only to certain lines of

neodymium. Some of the most conclusive evidence for solvation in solution, furnished by our spectroscopic work, was with the uranous salts.

The spectrum of uranous chloride in water is quite different from the spectrum in methyl alcohol, and this, in turn, very different from the spectrum in acetone. A glance at the plate for these solutions would lead us to conclude that we were dealing with three very different absorption spectra.

In a mixture of water and methyl alcohol, as the amount of water increases the water band $\lambda 6750$ comes out, gradually increasing in intensity. The methyl alcohol band $\lambda 5050$ to $\lambda 4850$ which is probably double, narrows on the red side into a band at $\lambda 4850$. Methyl alcohol bands $\lambda 4770$ and $\lambda 4600$ practically disappear and $\lambda 4670$ becomes very weak. In their places appear the water bands $\lambda 4700$ and $\lambda 4550$. The methyl alcohol band, $\lambda 4300$ to $\lambda 4450$, becomes weaker and breaks up into a band at $\lambda 4400$ and a band at $\lambda 4280$. The methyl alcohol bands $\lambda 4230$ and $\lambda 4120$ apparently come together, as the amount of water present relative to methyl alcohol increases, and become the water band at $\lambda 4160$.

It is thus obvious that the aqueous solution shows very different absorption bands from the solution of uranous chloride in methyl alcohol.

The addition of ethyl alcohol to an aqueous solution of uranous chloride produces a marked change in the spectrum, the ethyl alcohol bands being very different from the water bands. As the amount of ethyl alcohol present relative to water increases, the ethyl alcohol bands come out and the water bands gradually disappear.

The addition of acetone to a methyl alcohol solution of uranous chloride brings out a number of "acetone" bands between $\lambda 6000$ and $\lambda 6500$. A strong absorption band also appears from $\lambda 6500$ to $\lambda 6800$. There is also an acetone band at $\lambda 5600$.

The addition of acetone to an aqueous solution of uranous chloride produces a marked change in the spectrum, the "acetone" bands being very different from the "water" bands. The acetone solution absorbs much less in the region $\lambda 6500$. The aqueous solution has a characteristic band at $\lambda 6750$. There are acetone bands at $\lambda 4920$, $\lambda 4750$, and $\lambda 4590$; and water bands at $\lambda 4980$, $\lambda 4700$, and $\lambda 4570$. The absorption of uranous chloride in ethyl alcohol is very similar to the absorption in methyl alcohol, as would be expected; the methyl alcohol bands being of slightly shorter wavelengths.

The absorption spectrum of uranous chloride in glycerol

was photographed, also when water was added to the glycerol solution.

The absorption spectrum in glycerol was found to be very different from what it was in water.

The absorption spectrum of uranous chloride in a mixture of methyl alcohol and ether was photographed. The methyl alcohol solution showed complete ultra-violet absorption to wave-length $\lambda 3700$. The addition of ether increased the absorption, the absorption of the short wave-lengths extending now to $\lambda 3800$.

In methyl alcohol there was considerable general absorption in the region $\lambda 4300$. With the addition of ether the absorption was almost complete from $\lambda 4100$ to $\lambda 4450$. The addition of ether caused the uranyl bands to shift slightly towards the red without, however, changing their general character. The magnitude of this shift can be seen from the following table.

Uranyl chloride bands in methyl alcohol.

$\lambda\lambda$	3880,	4000,	4110,	4240,	4400,	4610,	4780,	4930,	5050,
			4135,	4285.					

Uranyl chloride in methyl alcohol to which ether is added.

$\lambda\lambda$	3890,	4010,	4140,	4260,	4440,	4630,	4790,	4960,	5050.
------------------	-------	-------	-------	-------	-------	-------	-------	-------	-------

The effect of the presence of ether is thus very pronounced, not only causing the bands to shift slightly towards the red, but also increasing the amount of absorption.

It should be stated that in the work with the uranous salts, there were present in the solution in addition to the salt a little of the free acid of the salt and a small amount of the zinc salt. While these probably had a slight effect on the absorption spectra, the effect must have been far too small to have produced such changes as those recorded above for the different solvents.

Having found such abundant evidence for the effect of the solvent on the power of the dissolved substance to absorb light, in the case of the few solvents referred to above, it seemed very desirable to bring other solvents within the scope of this work, and this has been done. Since the neodymium lines and bands are very sharp, it was selected as the principal substance to be used in studying the effect of the solvent on the absorption spectra of the dissolved substance, where a large number of solvents was to be employed. This phase of the work has been very recently carried out by Jones and Strong.

Absorption Spectra of Neodymium Salts.

The following nomenclature will be used in describing the neodymium absorption spectra.

α group in the region λ 3400 to λ 3600.

β „ at about λ 4300.

γ „ from λ 4600 to λ 4800.

δ „ from λ 5000 to λ 5400.

ϵ „ in the region λ 5800.

ζ „ at λ 6300.

In designating the neodymium spectra we start from the violet end of the spectrum. This is the natural method when a grating is used. It is doubtful whether, in the near future, the ultra-violet spectrum of neodymium can be studied much farther than we have done, so that this is the natural end of the spectrum at which to begin. It is, on the other hand, probable that there are many neodymium bands farther down in the infra-red than we have gone; and when these have been worked out they can then be named in the natural order.

The change in the absorption spectrum of neodymium chloride as the solvent is changed can be seen best by expressing the results in the following form. The abbreviations used are: "d" diffuse, "fa" faint, "fi" fine, "h" hazy, "i" intense, "n" narrow, "sh" sharp, "st" strong, "we" weak, "wi" wide.

The following results (pp. 738-9) obtained with neodymium chloride show the effect of the solvent on the absorption spectra of solutions of this compound. The bands of the different solvents have different wave-lengths and different relative intensities.

Having found that the solvent played an important part in determining the absorption of light by the dissolved substances, Jones and Strong used *isomeric organic solvents* to see whether such closely related compounds would affect differently the power of substances dissolved in them to absorb light. They prepared solutions of neodymium chloride in propyl and isopropyl alcohols, and in butyl and isobutyl alcohols, and photographed the absorption spectra of this salt in these isomeric solvents. The following results show different absorption lines and bands in the isomeric solvents.

Phil. Mag. S. 6. Vol. 23. No. 137. May 1912. 3 C

α Group.

In water.	In methyl and ethyl alcohols.	In propyl alcohol.	In isopropyl alcohol.	In butyl alcohol.	In isobutyl alcohol.	In glycerol.
λλ 3390 we. 3465 n. st. 3505 n. st. 3540 n. st. 3560	λλ 3475 fa. 3505 3560 wi. i.	λλ 3545 sh. 3460 3490 3510 we. 3525 st. 3540 st. n. 3560 d. 3580 we.	λλ 3460 3510 3535	λλ 3450 sh. n. 3460 we. 3492 d. 3535 sh. n. 3545 3560 d.	λλ 3455 we. 3485 st. 3515 we. 3545 3570	λλ 3520 we. 3475 st. 3550 st.

β Group.

In water.	In methyl and ethyl alcohols.	In propyl alcohol.	In isopropyl alcohol.	In butyl alcohol.	In isobutyl alcohol.	In glycerol.
λλ 4271 sh. 4290 n. we.	λλ 4290 4325	λλ 4270 we. 4285 4330 wi. we. 4450 wi. we.	λλ 4265	λλ 4265 4285 4300	λλ 4300 we.	λλ 4288 sh. 4270 fi. 4305 fi.

γ Group.

In water.	In methyl and ethyl alcohols.	In propyl alcohol.	In isopropyl alcohol.	In butyl alcohol.	In isobutyl alcohol.	In glycerol.
λλ 4610 h. 4645 we. 4685 4755 sh. 4820 ni.	λλ 4700 4780 4825	λλ 4600 we. d. 4700 4770 4830	λλ 4600 d. 4690 4730		λλ 4700 4730 4780 4830 4880 we.	λλ 4620 4710 4730 4760 4790 4840

δ Group.

In water.	In methyl and ethyl alcohols.	In propyl alcohol.	In isopropyl alcohol.	In butyl alcohol.	In isobutyl alcohol.	In glycerol.
$\lambda\lambda$ 5090 n. 5125 wi. h. 5205 i. n. 5222 i. n. 5255 n. 5315 fa. h.	$\lambda\lambda$ 5125 h. 5180 h. fa. 5220 i. n. 5245 i. 5290 n. 5315 fa.	$\lambda\lambda$ 5130 wi. d. 5180 wi. d. 5220 5230 5250 5290 5330 we.	$\lambda\lambda$ 5100 wi. d. 5320 wi. d.	$\lambda\lambda$ 5085 n. 5095 n. we. 5130 5200 5215 5240 5270 5300	$\lambda\lambda$ 5150 5260 5215 5230 5250 5300	$\lambda\lambda$ 5120 wi. h. 5170 n. 5190 n. 5230 5240 5250 5270 we.

ε Group.

In water.	In methyl and ethyl alcohols.	In propyl alcohol.	In isopropyl alcohol.	In butyl alcohol.	In isobutyl alcohol.	In glycerol.
$\lambda\lambda$ 5725 n. st. 5745 st. 5765 st. 5795	$\lambda\lambda$ 5725 h. 5765 n. 5800 st. 5835 i. 5860 h. 5895 fa. 5925 fa.	$\lambda\lambda$ 5740 5780 5810 5850	$\lambda\lambda$ 5720 d. 5780 5810	$\lambda\lambda$ 5750 5780 5820 5860 5900 5930	$\lambda\lambda$ 5740 we. 5810 st. 5850 st. 5890 5920 5950 we. 5995 we. 6020 we.	$\lambda\lambda$ 5740 h. 5790 5805 5820 5850

If we compare carefully the spectra of neodymium chloride in butyl and isobutyl alcohols, we find that the bands are weak and diffuse in isobutyl alcohol, and have different relative intensities from what they have in the butyl alcohol. The bands in butyl alcohol are very much finer and sharper than they are in isobutyl alcohol. Further, the bands of neodymium chloride in isobutyl alcohol have slightly greater wave-lengths than in butyl alcohol.

To eliminate the possibility of the effect of the solvent on absorption spectra being due to anything inherent in the nature of neodymium chloride, the nitrate of neodymium was studied in the same way as the chloride.

The absorption spectra of neodymium nitrate in water, in methyl alcohol, in ethyl alcohol, in mixtures of these alcohols and water, in propyl and isopropyl alcohols, in butyl and isobutyl alcohols, in acetone and in mixtures of acetone and water, in ethyl ester and in formamide, were carefully photographed and studied. Results will be given in the case of neodymium nitrate only for the α bands.

α Bands.

In water. Practically the same as the bands of neodymium chloride, but the bands of the nitrate are broader and hazier than those of the chloride.

In methyl and ethyl alcohol. There are only two bands in the α group, λ 3465 and λ 3545.

In propyl alcohol. $\lambda\lambda$ 3455, 3500, and 3585.

In isopropyl alcohol. $\lambda\lambda$ 3460, 3505, and 3535.

In butyl alcohol. $\lambda\lambda$ 3450, 3500, and 3540.

In isobutyl alcohol. Ultra-violet absorption was so great that on the plate taken the α group did not appear. The absorption in general is the same as that of the chloride in this alcohol.

In acetone. $\lambda\lambda$ 3475 and 3555.

In ethyl ester. $\lambda\lambda$ 3455, 3500, and 3540.

The other groups of absorption bands of neodymium nitrate in the different solvents show differences in the wave-lengths comparable with the above; but these results suffice to show the effect of the solvent on the power of neodymium nitrate to absorb light.

The above evidence that the solvent plays an important part in the absorption of light by substances dissolved in it is strong. When we take into account the number of salts studied and the number of solvents employed, the evidence

is little short of proof. The only reasonable question is how are we to interpret these facts? Before attempting to answer this question we should take into account also the following fact. We have seen that a salt dissolved in a given solvent is characterized by a definite absorption spectrum. When a salt is dissolved in mixtures of varying proportions of two solvents *only two definite absorption spectra appear*, one being characteristic of each solvent. One spectrum does not gradually change into the other as the composition of the mixed solvent changes, but only the *relative intensities* of the two spectra vary. Starting with that mixture of the two solvents in which both of the spectra are equally intense, if we diminish the amount of *a* relative to *b*, the spectrum corresponding to *a* becomes feebler and feebler, and the spectrum corresponding to *b* more and more intense. This fact was first noted by Jones and Anderson, and since repeatedly confirmed by the work of Jones and Strong. We found that when neodymium chloride is dissolved in a mixture of methyl alcohol and water, it showed a definite set of "water" bands and a definite set of "methyl alcohol" bands. As the amount of water in the solution was decreased relative to the alcohol, the "water" bands decreased in intensity but remained in the same position. As the amount of alcohol in the solution was decreased relative to the water the "alcohol" bands decreased in intensity, but their position remained unchanged.

Jones and Anderson interpreted these facts as strong evidence in favour of the view that there are definite hydrates and definite alcoholates in the solution.

The spectroscopic evidence for solvation in solution furnished by Jones and Anderson has, as has already been stated, been increased many fold by the work of Jones and Strong. A large number of solvents and a fairly large number of salts have been used, and the existence of solvent bands in general established.

The question of the relative stability of the different solvates with respect to various physical and chemical agents has been studied at length by Jones and Strong by means of absorption lines and bands. It would lead us beyond the scope of this paper to discuss these results in detail. Suffice it to say that the hydrates in general are the most persistent of all the solvates, although this depends upon the conditions to which the solution is subjected.

Taking all of the spectroscopic work into account, I regard the evidence from this source as strongly supporting the solvate theory of solution as advanced in this laboratory more

than a dozen years ago. The bearing of this theory upon Chemistry and other branches of Natural Science has already been pointed out*. Suffice it to say here that the solvate theory of solution is not at all at variance with the theory of electrolytic dissociation, but beautifully supplements it.

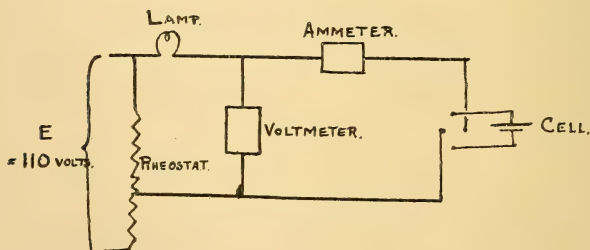
Johns Hopkins University, 1911.

LXX. *The Unilateral Conductivity of Sulphated Accumulator Plates.* By ROBERT G. LUNNON, B.Sc.†

THE high electrical resistance of accumulator plates which have been left unused for a considerable time is well known, and is due to the presence of a film of a sulphate of lead on the negative plate. This resistance becomes normal on the application of a high potential for a few minutes, and the experiments to be described were carried out to investigate this change. This object was attained, and it was further found that the layer of sulphate exhibits the property of aluminium anode-films in having a resistance dependent upon the direction of the current.

The accumulators used were of the simplest Planté type, as used in large numbers for obtaining a high potential. A different plate was necessarily used for each experiment, but the properties of the cells in one tray were found to be sufficiently identical to make this of no consequence. The connexion between the rate of decrease of the resistance and the applied potential difference was examined by including

Fig. 1.



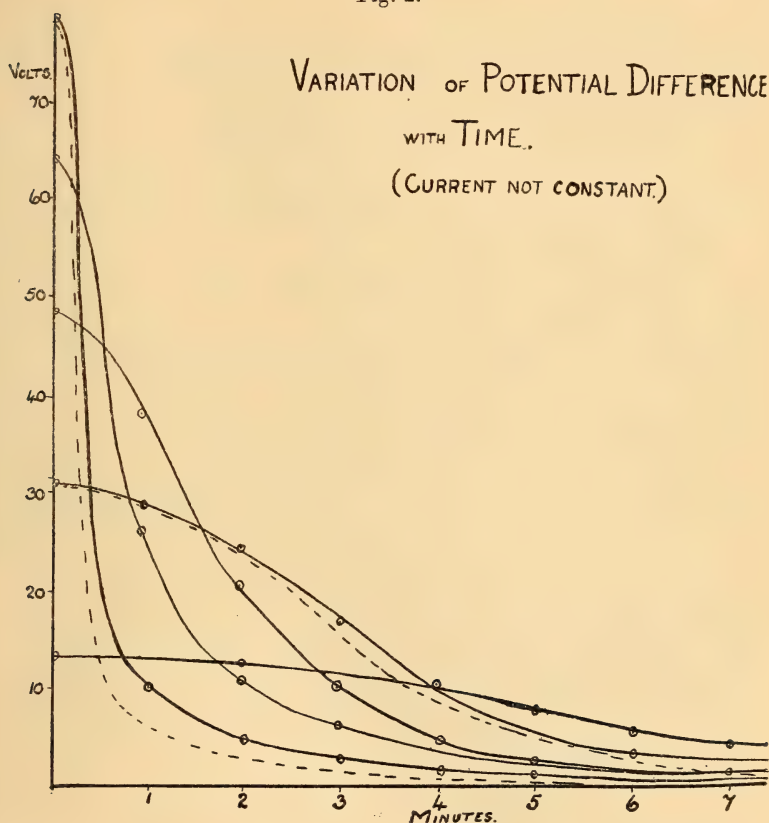
the cell in a circuit, as shown in fig. 1. With this arrangement, any desired p.d. could be initially applied to the cell, and its diminution with time, together with the current going

* *Zeitschr. phys. Chem.* lxxiv. p. 377 (1910). *Journ. d. Chim. phys.* ix. p. 217 (1911). *Amer. Chem. Journ.* xlv. p. 146 (1911).

† Communicated by Prof. F. T. Trouton, F.R.S.

through the cell, recorded. The curves so obtained are the continuous curves of fig. 2.

Fig. 2.



If V denote the potential measured by the voltmeter, we have

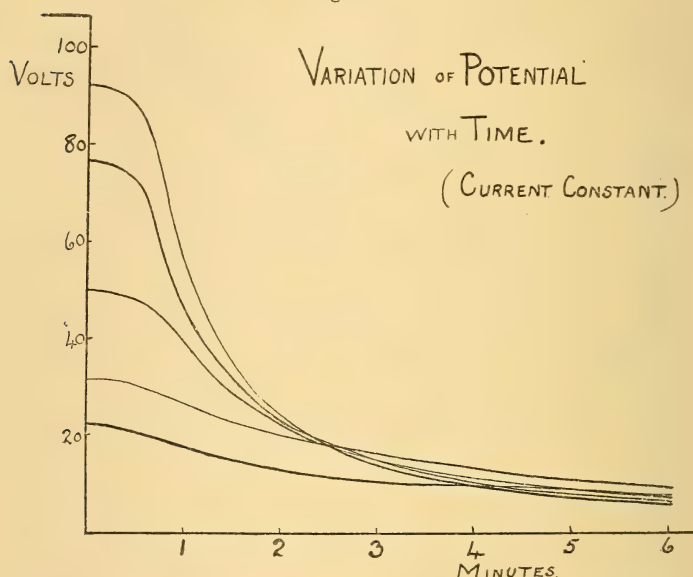
$$V = CR - E',$$

where E' is any back e.m.f. that may arise in the cell. No evidence could be found of a larger back e.m.f. than the two volts which develops when the cell is charged. Cook* has suggested the presence of a back e.m.f. to explain the properties of the aluminium anode-film, but this is not now generally accepted. Accordingly the variation of R with t may be found by keeping constant the current through the cell, or by dividing values of V by simultaneous values of C .

* Cook, Phys. Rev. xviii. p. 23 (1904)

The curves so obtained are given in fig. 3; they are, except at first, approximately exponential.

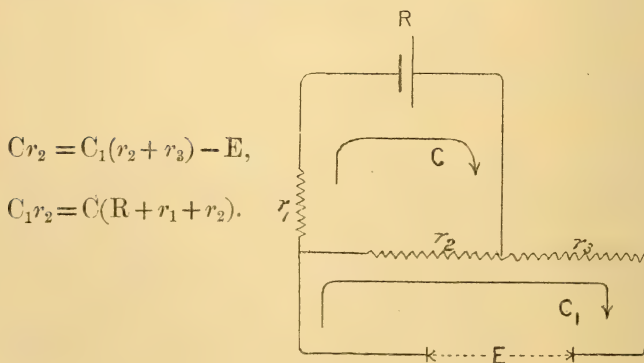
Fig. 3.



These results can be explained on the assumption that the resistance is proportional to the amount of substance on the electrode, and that the rate of removal of the latter is proportional to the applied p.d. The relation between V and t can then be obtained as follows:—

With the symbols of the diagram (fig. 4), we have

Fig. 4.



$$Cr_2 = C_1(r_2 + r_3) - E,$$

$$C_1r_2 = C(R + r_1 + r_2).$$

$$\therefore C = \frac{Er_2}{(R + r_1 + r_2)(r_2 + r_3) - r_2^2}.$$

$$\therefore V = RC = \frac{R}{AR + b},$$

where

$$A = \frac{1}{E} \left(1 + \frac{r_3}{r_2} \right), \quad b = \frac{1}{E} \left(r_1 + r_3 + \frac{r_1 r_3}{r_2} \right).$$

$$\begin{aligned} \therefore \frac{dV}{dt} &= \frac{b}{(AR + b)^2} \frac{dR}{dt} \\ &= \frac{b}{(AR + b)^2} \cdot (-k^2 V), \text{ if } \frac{dR}{dt} = -k^2 V, \\ &= -\frac{k^2}{b} V(1 - AV)^2. \end{aligned}$$

Integrating, and putting $V = V_0$ when $t = 0$, we obtain

$$\frac{V_0}{1 - AV_0} \cdot \frac{1 - AV}{V} = e^{\frac{k^2 t}{b} - \frac{1}{1 - AV} + \frac{1}{AV_0 - 1}},$$

or, with a new constant B ,

$$V = \frac{1}{A + Be^{\frac{k^2 t}{b} + \frac{1}{1 - AV}}}.$$

This equation is found to fit the curves of fig. 2 with considerable accuracy. Specimen curves plotted from it are given by the broken lines of the diagram.

In the case of constant current through the cell, we have

$$\frac{dR}{dt} = -k^2 V = -k^2 CR.$$

$$\therefore R = R_0 e^{-k^2 C t}.$$

This corresponds to the curves of fig. 3.

Finally, if we assume that the final resistance of the cell is always the same, since

$$\frac{dR}{dt} = -k^2 V,$$

$$\therefore R_0 - R_T = -K^2 \int V dt = \text{constant}.$$

Values of this integral can be obtained by computing the areas under the curves of fig. 3, and, as shown by the

following table, are approximately constant:—

Current.	$\int V dt.$
·73	638
·81	734
·90	696
1·11	803
1·43	646
1·60	785
2·36	720
Mean value 717	

In all the above experiments the current was sent in that direction for which the negatively formed plate is the anode. When the p.d. is applied in the reverse direction, the curve obtained for the decrease of V is similar in type, but the initial value, V_0 , is much lower, the reading is very unsteady, and visible sparking occurs at the cathode, apparently across the resisting film. The cell thus possesses, temporarily, the property of unilateral conductivity, offering a much larger resistance to a current sent outwards from the “formed” plate than to one in the reverse direction. The gas-layer theory developed by Schulze * for the corresponding property of the aluminium anode-film involves assumptions which are not possible in this case, and the more recent suggestion, of Corbino and Maresca †, of a perforation of the film of metallic salt is also unsatisfactory. The effect persists in the absence of any electrolyte; as, for example, in the case where the dry cathode with its film is pressed against a clean sheet of metal, and a current passed between the two. It is possible that the original electric deposition of the film involves a directional property in the substance of the film, which would not appear if the lead sulphate were chemically deposited; but, unfortunately, it has not been found possible to obtain a film deposited by chemical means alone to test this point.

A physical basis may be found for the assumption we have made regarding the rate of breaking down of the film, for we may consider that breaking down as a mechanical effect produced by the passage of electrons through the film. This effect would be proportional to the velocity of the electrons, and hence to the potential difference across the film, producing this velocity.

Physical Department,
University College, London.

* Schulze, *Wied. Ann.* xxi. p. 929 (1906).

† Corbino & Maresca, *Electrician*, Dec. 28, 1906.

LXXI. *The Recombination of Ions in Carbon Dioxide and Hydrogen at Different Temperatures.* By HENRY A. ERIKSON, Assistant Professor of Physics, University of Minnesota *.

IN a previous paper † it was shown that the rate of recombination of ions in air at constant density increases as the temperature of the gas is lowered. Results showing this were also obtained, in the case of air, by Phillips ‡.

In this paper are given the results the writer obtained some time ago for carbon dioxide and hydrogen.

The arrangement of the apparatus used was practically the same as described in the previous paper. The method consisted in measuring Q , the number of ions produced by the rays per second, and N , the number of ions of the same sign in the gas after the condition has been reached where as many ions are recombining per second as are being produced by the rays. The coefficient of recombination (α) was calculated from the relation $\alpha = K \frac{Q}{N^2}$, where K is a constant depending upon the dimensions of the ionization-chamber.

Carbon Dioxide.

The CO_2 used in the experiment was obtained from a commercial cylinder of the liquid, and was dried by passage through a coil imbedded in CO_2 snow.

In this gas also the coefficient of recombination of the ions was found to increase as the temperature was lowered from $+100^\circ \text{C.}$ to -64°C. The following are the average values obtained for N and α in arbitrary units :—

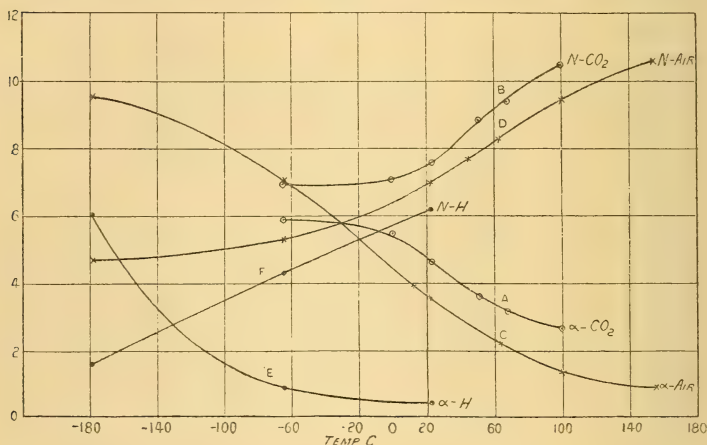
Temp.	N.	α .
100° C.	10.46	2.6
68	9.36	3.1
52	8.82	3.67
23	7.67	4.65
0	7.06	5.48
-64	6.95	5.89

* Communicated by Prof. Sir J. J. Thomson, F.R.S.

† Erikson, Phil. Mag. vol. xviii. p. 328 (1909).

‡ Phillips, Roy. Soc. Proc. Ser. A. lxxxiii. p. 246 (1910).

Curve A in the figure shows graphically the above values of (α) for carbon dioxide. Curve B shows how N varies with temperature. Q remains the same at all temperatures.



Curves C and D show the corresponding values previously determined for air.

Hydrogen.

The hydrogen used was obtained by the electrolysis of water, and was dried by passage through a coil immersed in liquid air.

In this gas also the coefficient of recombination was found to increase as the temperature was lowered, its value being thirteen times as great at -179°C. as at $+23^{\circ}$. The values obtained are as follows, the units being arbitrary:—

Temp.	N.	α .
23°C.	6.14	.45
-64	4.30	.90
-179	1.66	6.00

Curves E and F in the figure show the above values graphically.

The probable cause of the above variation in α is, it seems, the change in the thermal velocity of the ions as the temperature is altered. There is undoubtedly a relative velocity above which the ions cannot recombine. If we think of such

a definite limiting velocity, then the ions in a gas at any instant may be divided into two groups, in one of which only can recombination take place. If the temperature is altered, the number of ions in one group is increased and in the other is diminished. At a high temperature practically all the ions would have velocities greater than the limiting velocity and the coefficient of recombination, as well as its change with temperature, would be small. At a low temperature practically all the ions would have a velocity less than the limiting velocity, and the coefficient would be large. The values of α plotted against temperature would thus give a compound curve of the same character as the experimental curve.

Langevin's theoretical expression for α , namely

$$\alpha = 4\pi\epsilon(k_1 + k_2),$$

is also suggestive. In this expression $k_1 + k_2$ is the sum of the mobilities and ϵ is the ratio of the number of collisions that result in recombination to the total number of collisions between ions of opposite signs. The value of ϵ depends upon the lower of the two groups mentioned above.

By integrating Maxwell's expression for the distribution of molecular velocities between the limits zero and some limiting velocity, and dividing this by the same integral taken between the limits zero and infinity, we obtain the ratio of the number of ions having velocities less than the limiting velocity to the total number. If in the above integral the most probable velocity corresponding to different temperatures be used, we get the values of this ratio at these different temperatures. Substituting the square of the ratios thus obtained for ϵ in Langevin's expression, and considering the mobilities constant, we obtain a curve for the variation of α with temperature that is similar to the experimental curve at the higher temperatures, but is too steep at the lower temperatures. Kovarik * has shown, however, that at constant gas density the mobilities diminish at the lower temperatures. This brings about a closer agreement.

It gives me great pleasure to acknowledge my indebtedness to Prof. Sir J. J. Thomson and Prof. John Zeleny in connexion with this research.

Physical Laboratory,
University of Minnesota.
Sept. 20, 1910.

* Kovarik, *Phys. Rev.* vol. xxx. p. 415 (1910).

LXXII. *On Electric Currents in Air at Atmospheric Pressure, with Remarks on Induced Contact Electromotive Forces.* By Prof. A. ANDERSON, M.A., and H. N. MORRISON, B.Sc.*

IN 'The Theory of Ionization of Gases by Collision,' p. 80, Prof. Townsend seems to hold the opinion that it is impossible for a current of electricity to pass through the air space between two electrodes when the potential difference is as low as 30 volts, the air being at atmospheric pressure, even if the distance between the electrodes is less than the wave-length of sodium light. In support of this opinion, he refers to experiments made by Almy, who used spherical electrodes of about $\cdot 007$ cm. in diameter. The area of an electrode was, consequently, about the sixty-seventh part of a square millimetre, and if, as we believe to be the case, there are such currents, even for potentials much less than 30 volts, and for distances between the plates much greater than the wave-length of sodium light, it is hardly to be expected that they would be easily detected where such small electrodes are used. It is probable that such currents are due to the motion of electrons detached from the surface of one of the metals, and set in motion by the electric force between the electrodes; and, other things being the same, they would be proportional to the area of the surface from which the electrons are drawn. They cannot be explained by the drawing together of the opposing plates by the electrostatic force between them. In the apparatus used by us the electrodes were two parallel circular copper plates, the area of each being about 7 sq. cm. The upper plate was connected with one pair of quadrants of an electrometer and the lower with the positive pole of a battery of cells. Every precaution was taken to ensure insulation where insulation was necessary, and to guard against any effects other than that sought for. If the plates are at a distance of, say, $\cdot 005$ cm. and the potential of the lower plate be 30 volts, that of the upper plate being zero, the force between the plates will be about the weight of one-tenth of a gramme. No appreciable displacement of the plates could be produced by such a small force, and yet, under these conditions, there is a decided current. That these currents pass through the air seems to be put beyond doubt by another effect which takes place at the same time. Let the lower plate, B, be connected with the positive pole of the battery, and let the upper plate, A, which can be moved by means of a micrometer-screw be earthed. After a

* Communicated by the Authors.

short time earth both plates, and then insulate A and connect it with the electrometer, the plate B remaining earthed. A will charge up negatively, behaving exactly as if it were a plate of another metal electropositive to B when both are immersed in ionized air. This charging up of A cannot be accounted for by leakage through the insulating supports, as, in that case, it would charge up positively. It is therefore due to a contact difference and to the presence of carriers, both produced by the previous current through the air. There is no such effect when the plates are put into metallic contact and a current allowed to pass from one to the other. This induced contact difference is not permanent, but gradually diminishes and disappears after a time. Its magnitude and duration depend on the time during which B is in connexion with the battery and on the potential to which it is raised. If contact difference is to be explained by a difference in the amount of work done by an electron in escaping from a metal, then it would follow that when negative electrons have for some time been expelled from the surface of a metal, the effect is to lessen this work, that is, to make it easier for an electron to escape. This might arise through the removal of a layer of such electrons from the surface the presence of which would have the effect of preventing others from escaping. A similar induced contact difference is produced by the action of ultra-violet light, and may account for at least part, if not the whole, of the so-called photo-electric fatigue which metals exhibit when exposed to ultra-violet rays. It may be remarked that removing electrons from a metallic surface by means of a current, removing electrons by ultra-violet light, and cleaning the surface have similar effects on contact potential difference.

But currents can be produced between two plates of different metals under the action of their contact difference alone. Let the upper plate A be zinc and the lower plate B copper, and let the former be connected with one pair of quadrants of an electrometer and the latter earthed. Then, if the distance between the plates is about $\cdot 005$ cm., there will be no charging up of A observable, when the pair of quadrants with which it is in connexion is insulated. If the plates are in contact the same is true, and there is again no deflexion of the electrometer-needle. But if, starting from the position in which the plates are in contact, the plate A be gradually raised by means of the micrometer-screw a position is soon reached when a very rapid charging up of A takes place, the deflexion showing sometimes the whole contact difference, corresponding to a deflexion of 37 cm. on

the scale of the electrometer used, and sometimes less than this. A further separation of the plates by about the four-hundredth part of a millimetre will generally be sufficient to make the effect completely disappear; and if A be now gradually screwed down, the charging up of A will re-appear, and will be again entirely removed by bringing the plates into contact. The range within which this current is produced corresponds to about two divisions of the head of the micrometer-screw, that is to about .001 cm. Why the deflexion shows sometimes the whole of the contact difference and sometimes only part of it may be explained by assuming that when part only is shown there is metallic contact between the plates, whose resistance is comparable with the resistance of the air between the plates. Let the former resistance be R_1 and the latter R_2 . R_2 is the ratio of the current through the air to the potential difference between the plates, which for the sake of simplicity we will assume to be constant. If C denote the capacity of the pair of plates and the electrometer and V the contact difference, it is easy to show that the potential v indicated by the electrometer at a time t after the pair of quadrants in connexion with A is insulated is given by

$$v = \frac{R_1 V}{R_1 + R_2} \left(1 - e^{-\frac{R_1 + R_2}{CR_1 R_2} t} \right).$$

If R_1 is very small in comparison with R_2 , v will never acquire an appreciable value: but if R_1 be very great in comparison with R_2 , the final value of v will be V the contact difference. In general, the final value of v is $\frac{R_1 V}{R_1 + R_2}$. Experiments on the various points here referred to are in progress with a view of obtaining quantitative results.

LXXIII. *On the Deduction of Thermodynamical Relations.*
By Professor J. P. KUENEN, *University of Leiden* *.

IN a recent number of this journal † Dr. Houstoun deduces a relation between linear extension and torsion. At first sight this relation might seem to be incorrect, as in the proof no account appears to have been taken of the heat-effects which accompany the elastic changes. The author starts

* Communicated by the Author.

† R. A. Houstoun, *Phil. Mag.* [6] xxii. p. 740 (1911).

from the equation

$$dU = Fdx + Ld\theta, \dots \dots \dots (1)$$

where U is the energy, x the length, F the stretching force, θ the angle, and L the moment of the twisting couple. The complete equation, however, is

$$dU = Tds + Fdx + Ld\theta, \dots \dots \dots (2)$$

(s =entropy), from which (1) can only be obtained if $ds=0$, i. e. if the processes are supposed to be adiabatic. The author's intention is that the changes shall be isothermal, in which case (1) is incorrect. We obtain the correct expression by writing (2) in the form

$$d(U - Ts) = -sdT + Fdx + Ld\theta,$$

and putting $dT=0$, when it reduces to

$$d(U - Ts) = Fdx + Ld\theta.$$

As this equation is of the same form as (1), and as the further proof depends on the first side being a complete differential, the author's conclusions are all valid.

The same error in a different form is contained in the author's reasoning in connexion with the graphical proof of the relation in question: this method of proof was also used by the author in a previous paper * on magnetostriction, where a similar relation is deduced, and here the fallacy appears very openly. It is there explicitly stated, on page 82, that relations of the kind considered can be inferred from the principle of energy (first law) without using the second law at all. But the proof depends on the theorem that in an isothermal cycle no account need be taken of the heat-effects which cannot possibly be inferred from the first law: it can only teach us that the total heat-effect is equivalent to the total work, not that either of them disappears. This follows

from the second law $\int \frac{dQ}{T} = 0$, which for an isothermal cycle simplifies to $\int dQ = 0$; and this is the theorem in question.

In connexion with Dr. Houstoun's papers I wish to draw attention to a method of deducing thermodynamical relations which in these and many other cases affords considerable simplification. The usual method is starting from the entropy equation in its immediate form to deduce by the properties of complete differentials a relation between differential coefficients, and then by changing the variables put

* R. A. Houstoun, *Phil. Mag.* [6] xxi. p. 78 (1911).

the relation into the desired shape. These last transformations usually involve long and, as will appear, unnecessary calculation. The simplification in question consists in changing the variables in the original equation*.

The simplest case occurs when there is only one force to be considered. As an example I shall take a system under uniform pressure p . The fundamental equation is

$$Td s = du + p dv;$$

or bringing the complete differential du to one side,

$$du = Tds - pdv. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

By the property of complete differentials we have at once

$$\frac{\partial T}{\partial v_s} = - \frac{\partial p}{\partial s_s}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

one of the so-called "Maxwell's thermodynamical relations." The remaining three may be deduced from this one by changing variables, but much more simply by transforming the differential equation itself. If we subtract from both sides of equation (3) the differentials $d(Ts)$ or $d(-pv)$ or the sum of both, it assumes one of the following forms:

$$d(u - Ts) = -s dT - p dv,$$

$$d(u + pv) = Tds + v dp,$$

$$d(u - Ts + pv) = -s dT + v dp.$$

As the first side of each of these equations is again a complete differential, the remaining three relations follow immediately.

Incidentally this method makes it clear why there are four, and only four, relations of the simple form (4). At the same time it brings out very clearly why Gibbs introduced the three new thermodynamical functions $\psi = u - Ts$, $\chi = u + pv$, and $\xi = u - Ts + pv$, and no more.

The same method may be applied when there is more than one force to be considered: I will at once take the general case where there are n general coordinates $\alpha, \beta, \gamma \dots$ with corresponding forces A, B, C , the direction of the forces

* This method, though seldom applied, cannot be considered as new: it is virtually contained in Gibbs's treatise, and after writing this note I find that it is used in substantially the same form as here by G. H. Bryan, *Encyklopädie der Math. Wiss.* v. p. 1 (Teubner, 1903); but as it appears little known it may be useful to draw attention to it here.

being chosen in the positive direction of the coordinates. The entropy equation is then

$$du = Tds + A d\alpha + B d\beta + \dots$$

As before, we can transform this equation by subtracting from both sides one or more expressions like $d(Ts)$, $d(A\alpha)$, &c. As the second side has $n+1$ terms, it is easily seen that altogether 2^{n+1} equations may be written down; the above one included, each new form giving rise to the introduction of a thermodynamical function, so that including u there are 2^{n+1} of these.

The thermodynamical relations which follow from these equations are not all of the same kind: some of them involve the first term (Tds or sdT), others are between the remaining terms ($A d\alpha$ or αdA , &c.) mutually. The total number of relations deducible from each equation is $\frac{(n+1)n}{1 \cdot 2}$, of which $\frac{(n-1)n}{1 \cdot 2}$ are between the forces and coordinates with either of the two conditions $s = \text{const.}$ or $T = \text{const.}$ attached (these we shall call the elastic relations), and the remaining n (analogous to Maxwell's relations) containing s and T as variables. The total number of relations of the form considered is therefore $2^n n(n+1)$ involving $2^{n-1}(n-1)n$ adiabatic elastic relations, an equal number of isothermal elastic relations, and $2^{n+1}n$ of the Maxwell pattern.

It deserves notice that those relations in which amongst the constant quantities no coordinates occur such as the elastic relation

$$\frac{\partial \alpha}{\partial B_{TACD} \dots} = \frac{\partial \beta}{\partial A_{TB CD} \dots},$$

or the Maxwell relations

$$\frac{\partial s}{\partial A_{TB CD} \dots} = \frac{\partial \alpha}{\partial T_{AB CD} \dots} \quad \text{and} \quad \frac{\partial T}{\partial A_{sBCD} \dots} = - \frac{\partial \alpha}{\partial s_{AB CD} \dots}$$

are usually of more importance than the others, because as a rule experimentally forces are more easily kept constant than coordinates. It may also be remarked that in many problems which deal with only one or a few of the coordinates while the others are simply ignored, the relations which are obtained have all to be taken as involving the condition that these others, but more often the corresponding forces, remain constant.

In illustration of the method Dr. Houstoun's problems may here be solved. In the first we have :

$$dU = Tds + Fdx + Ld\theta,$$

which may be written as follows :

$$d(U - Ts - Fx - L\theta) = -sdT - x dF - \theta dL;$$

and therefore at once

$$\frac{\partial x}{\partial L_{TF}} = \frac{\partial \theta}{\partial F_{TL}}.$$

In the problem on magnetostriction the equation * is :

$$dU = Tds + Fdx + \frac{vH}{4\pi} dB,$$

which we write in the form

$$d\left(U - Ts - Fx - \frac{v}{4\pi} HB\right) = -sdT - x dF - \frac{vB}{4\pi} dH,$$

which yields the "elastic" relation

$$\frac{\partial x}{\partial H_{TF}} = \frac{v}{4\pi} \frac{\partial B}{\partial F_{TH}},$$

and two Maxwell relations

$$\frac{\partial x}{\partial T_{HF}} = \frac{\partial s}{\partial F_{HT}} \quad \text{and} \quad \frac{v}{4\pi} \frac{\partial B}{\partial T_{FH}} = \frac{\partial s}{\partial F_{TH}}.$$

The same problem was discussed by Heydweiller †, who takes into account the change of volume, and uses the equation

$$dU = Tds + Fdx + \frac{vH}{4\pi} dB + \frac{HB}{4\pi} dv,$$

or as before,

$$d\left(U - Ts - Fx - \frac{vBH}{4\pi}\right) = -sdT - x dF - \frac{vB}{4\pi} dH;$$

so that

$$\frac{\partial x}{\partial H_{TF}} = \frac{v}{4\pi} \frac{\partial B}{\partial F_{TH}} + \frac{B}{4\pi} \frac{\partial v}{\partial F_{TH}}.$$

* I follow Dr. Houstoun's equation without taking into account Dr. R. Gans's criticism of the equation itself (*Bebilätter*, xxxv. p. 717, 1911).

† Heydweiller, *Ann. d. Phys.* [4] xii. p. 602 (1903) : again I leave out of account the criticism by Dr. Gans, *l. c.* xiii. p. 634, xiv. p. 638 (1904).

The superiority of the above method will be realized when it is compared with the proofs of the equivalent relations by the authors named.

In the application of the second law to mixtures similar transformations of the differential equation are often useful. In that case the equation has to be supplemented by terms containing quantities which determine the amounts of the various components of the mixture. These terms may be of the form μdm , equal in number to the number p of the components, where m stands for the quantity (*e. g.* mass or number of gramme-molecules) of each component, and μ is called the potential (Gibbs). In many cases it is more appropriate to refer the equation to a definite quantity (*e. g.* unit mass or one molecule), and introduce variables which determine the composition of the mixture, *e. g.* the ratios $x, y, \dots$ of the amounts of the 2nd, 3rd, $\dots$ component to the whole; the equation then assumes the form

$$du = Tds + \sum A d\alpha + \sum^{p-1} X dx.$$

The total number of forms into which this equation may be put by the subtraction of expressions like $d(Ts)$, $d(A\alpha)$, or $d(Xx)$, is obviously 2^{n+p} , giving rise to the introduction of the same number of thermodynamical functions (including u itself) and allowing the deduction of $(n+p)(n+p-1)2^{n+p-1}$ thermodynamical relations of the special simple form under consideration. A further discussion of these relations or of the application of the functions *e. g.* for the construction of thermodynamical surfaces would be out of place here*.

LXXIV. The Action of Ultra-violet Light on Chlorine.

By E. B. LUDLAM, D.Sc.†

THE action of ultra-violet light upon many elements causes them to eject electrons, and the more electro-positive the element the more easily is the electron ejected. Thus, the alkali metals are the most sensitive to ultra-violet light and less positive metals less so; nevertheless, an element so electronegative as oxygen gas appears to be ionized by ultra-violet light, presumably by the detachment of an electron, as in the case of metals. It was therefore a matter of interest to ascertain whether chlorine, the most

* Compare H. Kamerlingh Onnes and W. H. Keesom, *Encyklopädie der Math. Wiss.* v., which is to appear shortly.

† Communicated by the Author.

electronegative element upon which we can experiment, showed any similar photoelectric effect.

Lenard has found that in the case of oxygen a shorter wave-length is necessary to produce ionization than is required to convert the oxygen into ozone. Shenstone carried out an experiment* to discover if any ozone-like modification of chlorine was produced by means of the silent electric discharge, but his result was purely negative.

Chlorine, being green, absorbs light in the visible portion of the spectrum, and there is no doubt that light of this wave-length is effective in producing chemical change. It was, therefore, of interest to ascertain whether any ionization of the gas was measurable when it was exposed to light of various wave-lengths, including such light as is effective in ionizing oxygen. In this connexion it is worthy of note that the spectrum of chlorine in the ultra-violet region does not consist of lines but of a band, and in this region the emission spectrum is not the same as the absorption spectrum; from this it may be anticipated that the mechanism of the absorption in the ultra-violet band is not the same as in the portion consisting of lines, and this band absorption might fully prevent the ejection of electrons.

But, of all the problems connected with chlorine, the most fascinating is the mechanism of its union with hydrogen under the influence of light. Under suitable conditions the union takes place with explosion, but, that this may occur, the gases must be mixed in equal volumes, they must be free from certain impurities which impede the reaction, the illumination must be powerful, and the gases must not be absolutely dry.

The actual amount of energy supplied by the light is negligible compared with that liberated by the reaction, therefore the light plays the part of the trigger to the explosion, and the new equilibrium which it sets up is not displaced by the energy supplied by the light.

It was mainly with a view to obtain some knowledge of the mechanism of this catalytic trigger action that the work described in this paper was undertaken, for one point of first importance to settle is the question as to whether light is capable of ionizing chlorine.

Before dealing with the actual experiments, it may be serviceable to state briefly some of the most recent results obtained by Lenard and his collaborators, as these have not yet appeared in a publication of wide circulation †.

* Shenstone, J. C. S. Trans. vol. lxxi, p. 487.

† See Lenard & Ramsauer, Trans. Heidelberg Academy, Aug. 2, 1910 to Aug. 4, 1911, five parts.

Long ago Lenard showed that the action of ultra-violet light on gases produced three kinds of effects * :—

1. The gas may conduct electricity owing to the production of positive and negative ions.
2. Condensation nuclei may be formed, devoid of electric charge †.
3. Chemical molecular change may take place (3O_2 to 2O_3).

All these effects are due to the action of the periodic electric forces on the molecules of the gas.

Nuclei.—The condensation nuclei persist longer than the ions, from which they can be separated by means of a powerful electric field; they are unaffected by cooling to $-70^\circ\text{C}.$, but destroyed at $180^\circ\text{C}.$; their diameter appears to be some 25 times that of the molecule of the gas, but varies with the duration of illumination, increasing with the time; their formation was at first thought to be analogous to the production of ozone, but is more probably due to secondary chemical reactions (e. g., NH_3 oxidized to NH_4NO_2 , &c.). When the gases, not specially purified by cooling, are exposed to short wave-lengths (below 180μ), there is no diminution in the number of condensation nuclei (as judged by means of a steam jet) whether the ions are removed by a powerful electric field or not. Hence the nuclei are more effective than ions in bringing about the condensation of supersaturated steam.

When, however, the gases are highly purified, most effectively by freezing out impurities by means of liquid air, no nuclei are formed, proving that they are due to minute traces of vapours present in the air; the effect of the merest traces of water vapour, ammonia, or vapour from rubber tubing is most striking.

Ions.—The production of ions of molecular dimensions is explained by supposing the loss of a negative electron by one molecule and the gain of it by another. Larger ions could arise by agglomeration, but this process does not go far, or by the attachment of a small ion to a larger particle (nucleus) suspended in the gas.

With gases not highly purified, the longer and more powerful the illumination the larger the ions, but with gases purified by cooling to $-78^\circ\text{C}.$ only ions of molecular size are formed; hence, it appears that large ions are due to the acquisition of an electron by a nucleus.

* Lenard & Wolf, *Ann. d. Phys. u. Chem.* vol. iii, F (1889); *Ann. d. Phys.* vols. i. & iii. (1900).

† See also C. T. R. Wilson, *Phil. Trans.* vol. xcii. (1899).

In this way the nuclei have the effect of conserving the ions, damping their velocity and so preventing their rapid recombination and diffusion to the walls*.

Ozone.—Is produced even in air which has been purified by cold and must be a consequence of the direct action of the light on the molecules of oxygen; its production is caused by wave-lengths longer than $200\text{ }\mu\mu$, and is not associated with any photoelectric effect.

Effect on the Walls of the Vessel.

All the experiments on ionization of gases are complicated by the action of the light on the walls of the containing vessel. No conductor is available for the walls which does not either give out ions itself, or contaminate the gases. The wave-length at which the wall-effect begins is longer than that at which the gas effect first takes place; further, the ions produced are always negative, whereas the gas effect produces an equal number of positive and negative ions; consequently, the excess of negative ions over positive is throughout these experiments ascribed to the action of light on the walls of the vessel.

Wave-length.—A careful study of the effects observed through different media leads to the conclusion that the difference in properties between visible violet and the adjoining ultra-violet is less than between some portions of the ultra-violet region, and this may account for numerous discrepancies between the results of different observers who have unwittingly been experimenting with light of different wave-lengths.

Experimental.

The source of light employed was a spark of about one centimetre in length produced between aluminium terminals connected to a coil of special construction, wound with a secondary of low resistance and provided with a condenser of great capacity. The coil was supplied with a current of 20 amperes broken by a Wehnelt interrupter. The coil and spark-gap were both enclosed in tin boxes connected to earth.

Chlorine is a difficult gas to work with. Accordingly, the plan followed was to commence with air, to observe the effects already established with regard to it and proceed to examine the effect of an increasing proportion of chlorine, until pure chlorine itself was under investigation; then, to add intentionally certain vapours and note their effect.

* The reverse action, destruction of ions, has been observed in cases where the concentration of the nuclei was very great.

Table of Wave-lengths in the Ultra-violet Region.

Wave-length. $\mu\mu$		Description and abbreviation.	Remarks.
440—380	Intraquartz-violet;	Violet.	Visible.
380—340		Glass Ultra-violet (Glass-violet).	Passes through ordinary glass (in fairly thin layers); Carbon arc rich source.
340—300		Jena glass Ultra-violet (Jena-glass * violet).	Passes through Jena ultra-violet crown glass; strongly emitted by the Uviol Mercury lamp.
300—220		Quartz-glass Ultra-violet (Quartz-glass * violet).	Passes through fused silica (and calc-spar) in fairly thin layers; last portion of strong radiation from the Quartz Mercury and Amalgam lamps.
220—180		Quartz-crystal Ultra-violet (Crystal-violet).	Passes through crystallized quartz, gypsum, rock-salt in fairly thin layers: separable in the quartz- spectrograph.
180—120	Transquartz-violet.	Fluorspar Ultra-violet (Schumann- violet).	Passes through good fluorspar, but completely absorbed by a short space of air; separable in a vacuum—fluorspar—spectro- graph.
120—90 (?)		Reflex ultra- violet (Reflex violet).	On the dispersion theory strongly reflected by the above media; separable by means of a reflexion grating.
Shorter waves		Trans-reflex Violet.	

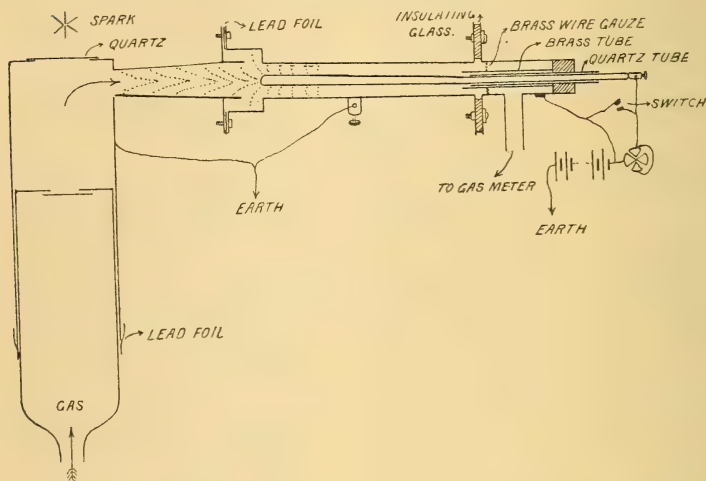
* These two radiations are by no means sharply separated by the absorption of fused quartz, this absorption increasing very gradually in the region of $220 \mu\mu$; nevertheless, it may be convenient to reserve separate names for the two portions of quartz-violet.

In early experiments the chlorine was obtained respectively from chlorine water, bleaching powder and sulphuric acid and by the electrolysis of cupric chloride solution, but finally the gas was obtained from liquid chlorine in a steel cylinder.

The gas was dried by passage first over calcium chloride, then over phosphorus pentoxide on broken glass, and finally

through a filter of purified asbestos in a Jena-glass tube which could be rendered absolutely free from moisture by heating in the blowpipe to a bright red heat.

Diagram of Connexions.



The gas then passed into the brass illuminating vessel, of which the walls, in the later experiments, were gold-plated. It was led in front of a window of crystalline quartz, $\frac{1}{4}$ mm. thick, and thence into a cylindrical condenser of the type described by Becker*. The illumination vessel and the outer cylinder of the condenser were earthed, the axial rod of the condenser was connected by protected wires to the two quadrants of an electrometer, whose sensitiveness was arranged so that one volt gave a deflexion of 300 mm. on the scale. The electrometer case and the metal box in which it was placed were connected with one pole of a high-potential battery whose other pole was earthed. The small battery used for charging the needle, and the high-potential battery, were also both enclosed in earthed metal boxes to prevent possible disturbances arising from the sparking in the neighbourhood.

In the earlier experiments the condenser was made entirely of brass, the insulating parts being of special glass, but later brass which had been gold plated was used, and in the concluding experiments both the cylinder and inner rod were of carbon, insulated by means of fused quartz.

From the condenser the gas passed into a gas meter of

* *Zeitschr. für Instrumentenkunde*, vol. xxix. p. 258 (1909).

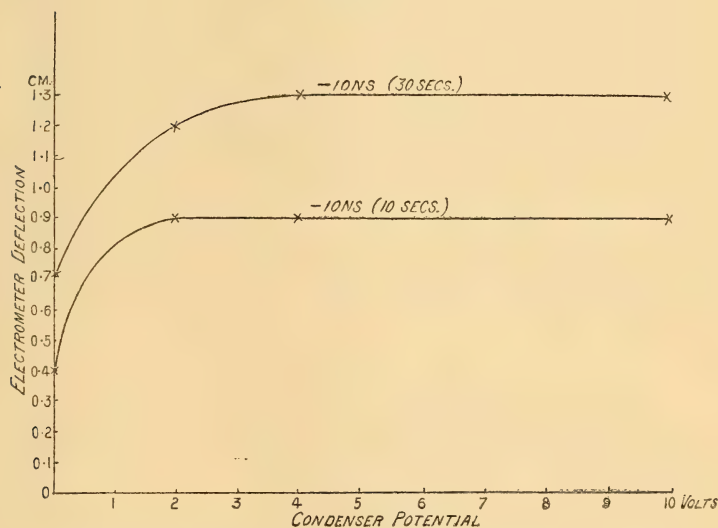
very simple construction and thence into a large carboy containing slaked lime, and from this away into the open air. An electric fan was employed to maintain a strong draught and remove such chlorine as might leak into the air.

The series of curves show the kind of result obtained :—

Experiments on Air.

Curve I.—Represents the results of one of the earliest experiments using ordinary pure dry air. It shows how all the negative ions produced by 10 seconds' illumination were caught by a potential difference of two volts, but that with

Curve I.



Effect of duration of illumination on the number and mobility of negative ions in air.

three times the illumination larger ions had been formed requiring four volts before the saturation potential was reached, only about 90 per cent. of the ions being caught at 2 volts.

From the formula deduced for his condenser by Becker*, the velocity of the ion corresponding to a saturation potential of two volts works out to 0.28 centimetre per second for one volt per centimetre, and for four volts half that velocity. The formula is, however, only an approximation unless a radial field is secured inside the condenser and the stream of gas is free from eddies, whereas in these experiments such

* A. Becker, *Ann. de Phys.* vol. xxxi, p. 98 (1910).

was not the case. The Becker condenser is admirably suited to the measurement of the mobility of large slow-moving ions, but suffers from the disadvantage that a very perceptible loss of the smaller ions takes place by recombination and diffusion to the walls of the apparatus before the condenser is reached. To avoid this the radial field was sacrificed by adopting an unusual system of electrical connexions whereby all the ions of the required sign were drawn towards the axial rod of the condenser which was connected to the electrometer.

Influence of the rate of flow of the gas on the number of ions carried into the condenser.—Compressed air from a cylinder was driven at various speeds through the apparatus and the deflexion due to the negative ions was measured. The number of positive ions was so small in comparison with the negative ions that the latter could be regarded as all produced by the action of the light on the walls, and therefore constant, thus the complication arising from the fact that with increased speed more gas is exposed to the action of the light was avoided. With a speed of 1 litre per minute the deflexion was 1.5 cm., with 3 litres per minute this had increased to 4.2 cm., and to 8 cm. at 5 litres per minute. In consequence of this result a rapid stream of gas was employed in all the later experiments.

Experiments on Chlorine.

A current of air at a speed of four litres per minute was sent through the apparatus, and chlorine in gradually increasing amounts was mixed with it.

When no chlorine was present very few positive ions were formed, nor was there any marked increase when 0.5, 1.5, 15, and 90 per cent. chlorine were added, the velocity of the mixed gases being always 4 litres per minute.

With the pure chlorine the deflexion was hardly measurable at all (velocity 3 litres per minute, as the meter would not measure more of the heavy gas).

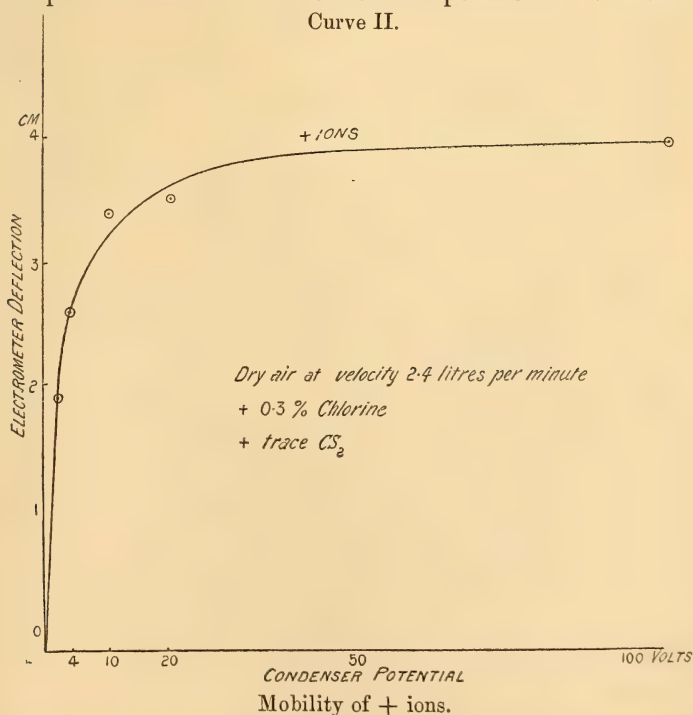
The addition of very *small* quantities of chlorine (less than .5 per cent.) to pure air was found in some early experiments to diminish the number of negative ions and increase the number of positive ones. The decrease in the negative ions was to be expected, for their number is swelled by the presence of ions from the walls of the vessel, and these are fewer when the light has to traverse a powerfully absorbing gas before striking the walls.

Influence of a Trace of Carbon Disulphide.

It was found that when the proportion of chlorine was increased beyond about 1 per cent. the number of positive ions began to decrease. It was considered possible that this might be due to increase in the rapidity of recombination accompanying increase in concentration, and accordingly a series of experiments was conducted in which a trace of carbon disulphide was allowed to diffuse into the air containing chlorine, for Lenard had found that this substance, under the influence of ultra-violet light, furnished nuclei capable of conserving the ions.

With air containing only a trace of carbon bisulphide the number of ions produced was only slightly greater than when pure air was employed, but immediately chlorine was added the effect was very marked, a decided increase taking place in the number of positive ions formed.

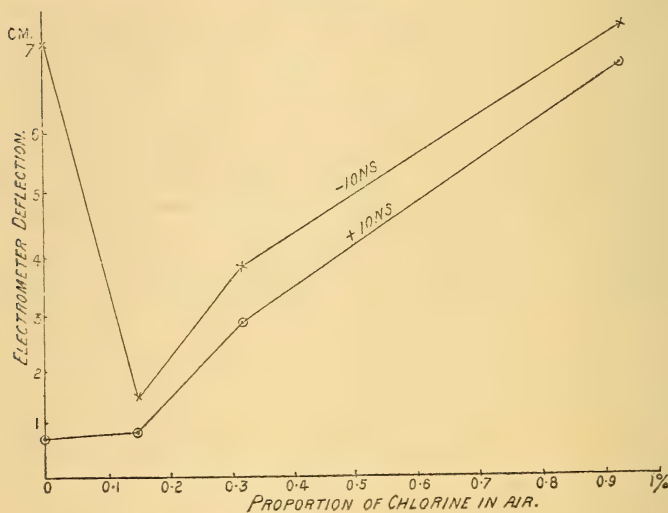
Curve II.—Shows a typical example of the results obtained for positive ions in this series of experiments. It will be



noticed that the curve begins to run horizontally at about 30 volts, signifying that much larger ions are present than in Curve I., moving with less than one tenth the speed.

Curve III.—The effect of gradually increasing the proportion of chlorine is shown in a striking manner in Curve III. With no chlorine at all, the negative ions are greatly in excess of the positive, but, directly so little as 0.15 per cent. is added, the number drops to one fifth its previous value, and approximates to that of the positive ions.

Curve III.



Influence of small per cent. of chlorine on the ionization of air.
(Potential = 100 volts.)

With further increase in the quantity of chlorine, both positive and negative ions increase in number side by side, the negative being always slightly in excess.

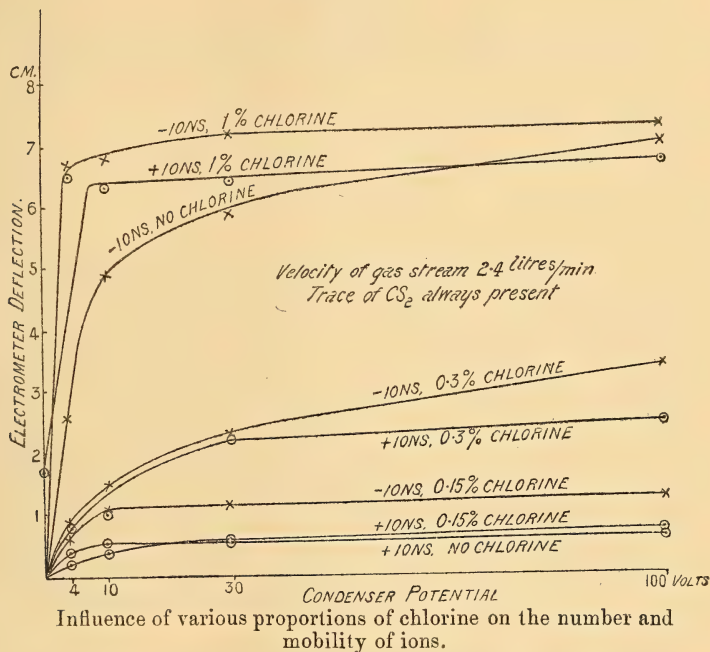
In this series of experiments the potential was not varied, being maintained at 100 volts, as previous results had indicated that 100 volts was more than sufficient to catch all the ions. However, to follow any changes which might have taken place in the size and mobility of the ions due to the addition of chlorine, a series of experiments was carried out of which the results are represented in Curve IV.

Curve IV.—The most striking fact indicated by this curve is the small size of the ions produced in the presence of 1 per cent. of chlorine—the two highest curves may be said to run horizontally from a potential of 4 volts, for 0.3 per cent. chlorine, 30 volts were necessary to catch all the positive ions—a value in agreement with Curve II.

The curve also shows that the first effect of a small quantity of chlorine (0.15 per cent.) is to increase the size of the ions, for with no chlorine present all are caught at 10 volts; with

0.15 per cent. chlorine 30 volts are necessary. The drop in the number of negative ions on the first addition of chlorine is again very clearly brought out.

Curve IV.

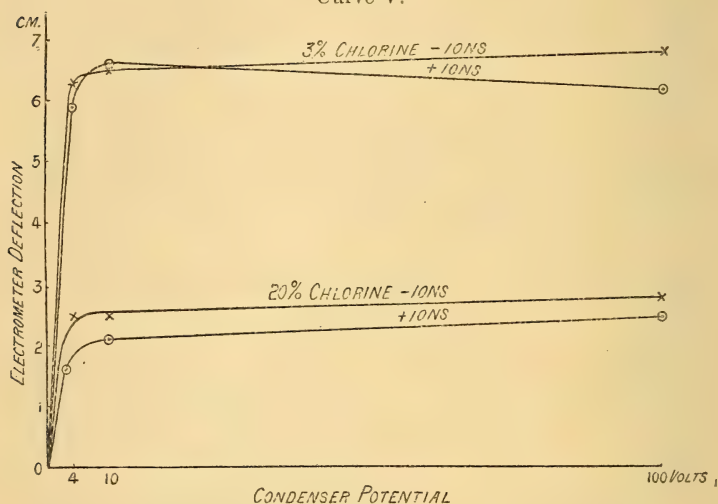


Curve V represents the effect observed with increased percentage of chlorine. The number of ions in 3 per cent. chlorine is pretty much the same as was found in air containing only 1 per cent., but when the chlorine is increased to 20 per cent. the ionization drops to about one third the value. This result might have been attributed merely to the increase in the rate of recombination due to the absence of sufficient diluting gas, but another possibility suggested itself, namely, that the stream of cool air drawn past the apparatus by the fan had so lowered the temperature of the carbon bisulphide tube as to reduce its vapour pressure below the minimum necessary to provide a sufficient number of nuclei to efficiently conserve the ions, now that the proportion of chlorine was very considerable. Consequently, the experiment was repeated with the carbon bisulphide tube immersed in water at 27°C ., whereupon the number of ions was almost trebled*. This result opened the question as to whether the

* V.P. of CS_2 { 10° 20° 27°
 20 cm. 30 cm. 40 cm. approximately.

effect observed might not be due to a chemical action between the chlorine and the carbon bisulphide under the influence of the light.

Curve V.



Influence of greater per cent. of chlorine on ions produced in air.

If this were the case, the presence of a large excess of chlorine would result in the absorption of the light by the chlorine without production of ions before the photo-chemical action could come into play.

Wave-length.—Throughout each series of experiments observations were made upon the wave-length of the light producing the various effects, and similar results were always obtained, of which the table below is characteristic.

Air at the rate of 2.4 litres per minute, chlorine 1.5 per cent., trace of carbon bisulphide.

Medium between Spark and Gas.	Deflexion	
	+	-
3 cm. air, $\frac{1}{4}$ mm. quartz	100	100
„ „ 3 mm. gypsum (fine split crystal plate)	81	77
3 cm. air, 3 mm. gypsum (old and rubbed)	10	10
3 cm. air, calc-spar	2*	8
3 cm. ultra-violet crown glass	4	4
Violet crown glass	0	2
Ordinary glass	0	0

* This is an unusually low value, 8 is nearer the average, although the positive deflexion was usually rather less than the negative when calc-spar was used.

The plate of gypsum, examined in the quartz spectrograph, was still very transparent to wave-lengths of 185μ ; the calc-spar had a sharp boundary, being transparent to wave-length 206μ , but opaque to 202μ ; the ultra-violet crown glass absorbed all shorter than 290μ . The evidence is sufficient to warrant the conclusion that, for any considerable ionization, wave-lengths shorter than 200μ are required, and if any ionization is caused by light which can pass through any considerable thickness of glass, the amount can hardly be within our means of measurement.

Schumann Violet.

In all the experiments hitherto described, the light traversed at least two centimetres of air and a quarter millimetre of quartz before reaching the gas. In order to see whether any effect was produced by rays of still shorter wave-length, such as air and quartz powerfully absorb, a different illumination vessel was used, made of brass and closed by a plate of fluor-spar. The spark-gap was placed within two or three millimetres of the window, from which it was separated by a shield of fused quartz pierced with a small hole about the same diameter as the window; the condenser cylinder and rod were of graphite, and the sensitiveness of the electrometer was reduced to about one half. The following series of results was obtained:—

	Deflexions cm.	
	+	—
(1) Air alone at 5 litres per minute.....	12, 13	29, 28
(2) Air + about 10 per cent. chlorine, 5 litres per minute.....	1, 1	—2, 4, 4
(3) Pure chlorine, 3 litres per minute	0	0
(4) Air alone, 5 litres per minute.....	12, 14	29, 26
(5) Air + 50 per cent. chlorine	0	0
(6) Pure chlorine, 3 litres per minute	0	0
(7) Air alone, 5 litres per minute.....	11	21, 17, 16

This was a long series of experiments, and the diminution in the effect observed with pure air towards the end of the series is easily explained by the fact that it is impossible to

Phil. Mag. S. 6. Vol. 23. No. 137. May 1912. 3 E

keep the surface of the fluorspar perfectly free from a deposit of aluminium given off by the sparks, despite brushing with a camel's-hair brush between each two successive illuminations.

The experiment is very conclusive in its evidence that the presence of chlorine destroys the conductivity produced in air, and that if pure chlorine itself is ionized it can only be so to a minute extent.

Effect of Moisture.—Carbon disulphide had been introduced into the earlier experiments to act as a conserving agent, but the experiments of Lenard had shown that traces of moisture were likely to act in a similar manner. In this connexion it is of great interest to remember that Baker found that the velocity of combination of hydrogen and chlorine exposed to bright light was very greatly dependent on the presence of a trace of moisture.

After passing over the usual drying apparatus and through the filter, the air was made to pass over a small surface of water, arranged by calibration to contribute about one gram of water vapour per cubic metre of air.

The results are tabulated below :—

Gas.	Deflexion cm.	
	+	—
Air alone (dry)	1.1	1.8
Air alone (moist)	15.0	15.9
Air + 10 per cent. Cl_2 (moist)... ..	0	0.2
Cl_2 alone (moist)	0	0
Air again („)	14.7	15.3

This table brings out two points very clearly.

- (1) The presence of a trace of water vapour enormously increases the action upon air—in the case of the positive ions the increase is more than ten-fold.
- (2) Even this increased effect is completely obliterated by chlorine.

Experiments with the Steam-Jet.

In conclusion it was a matter of interest and some importance to ascertain whether chlorine, in the various circumstances under which it had been examined, gave rise to condensation nuclei or whether it prevented their formation. For this purpose the gases on leaving the illumination vessel were made to impinge against an orifice from which a jet of steam was issuing. On sparking for a few seconds the production of a cloud of steam showed instantly whether nuclei were present.

The following table contains the result of the experiments, which were carried out in the sequence given.

		Diam. of nuclei. mm.
(1) Air alone without sparking.	A very feeble effect.	
(2) Air illuminated.	Very considerable effect, grey.	6×10^{-6}
(3) „ + CS ₂ .	Reddish brown cloud.	4×10^{-6}
(4) „ + CS ₂ + Cl ₂ .	Scarcely any.	
(5) „ + CS ₂ + H ₂ O.	Powerful effect, grey.	6×10^{-6}
(6) „ + CS ₂ + H ₂ O + Cl ₂ .	Scarcely any.	
(7) Pure Cl ₂ .	Very slight.	
(8) Air again.	Powerful effect, grey.	6×10^{-6}
(9) „ + Cl ₂ (2).	Scarcely any.	
(10) „ + Cl ₂ + CS ₂ .	Scarcely any.	

Thus it is seen that the results with the steam-jet fall into line exactly with those obtained by means of the electrometer, and indicate that chlorine forms neither ions nor nuclei, but that its presence is destructive of those otherwise produced in air. In this they confirm the experiments of Burgess and Chapman * as opposed to those of Bevan.

Conclusions.

The following effects have been confirmed or established :—
That under the influence of ultra-violet light,

- (1) There is very little ionization produced, even in ordinary air, by light of wave-length longer than $200 \mu\mu$.
- (2) That *pure dry* air is not greatly ionized by wave-lengths longer than $180 \mu\mu$, but with shorter wave-length the ionization is considerable.
- (3) That the addition of a trace of water vapour to air enormously increases the amount of ionization.
- (4) That the addition of very small quantities of chlorine to ordinary air increases the amount of ionization, but that with more chlorine the reverse takes place.
- (5) That pure chlorine is not ionized appreciably.
- (6) That pure chlorine does not form condensation nuclei.
- (7) That chlorine in considerable quantity destroys the ions and the nuclei otherwise formed in air.

* J. C. S. Trans. vol. xc. p. 1399 (1906).

These results point to the fact that the atom of chlorine does not easily lose an electron, and this is what might be expected from its electronegative character. Affinity for negative electricity is the characteristic of electronegative elements. Hydrogen is a borderland element, taking up a position among the noble metals in virtue of its electrochemical properties; it is distinctly more electropositive than copper, however, even at ordinary atmospheric pressure, and this is more marked at higher pressures. A possible explanation of the reaction between hydrogen and chlorine is that an atom of *hydrogen*, under the influence of ultra-violet light, emits an electron which immediately becomes attached to an atom of chlorine and chemical combination takes place*. There is some support for this hypothesis in the fact that the presence of hydrogen enormously increases the number of ions emitted by hot platinum and by the alkali metals at ordinary temperatures.

The fact that in many cases minute traces of foreign matter are requisite both for the ionization of gases and for their chemical combination is very striking; the two actions are probably either cause and effect or are attributable to some common cause. However this may be, it appears that actual liberation of electrons for any measureable period of time is not a necessary precursor of gaseous combination.

In conclusion I must express my indebtedness to Prof. Lenard for his kindness in allowing me to work in the Radiological Institute of the University of Heidelberg and for his guidance while the work was in progress. My thanks are also due to Prof. Becker and Dr. Ramsauer for kind assistance and advice.

Clifton College, Bristol.

LXXV. *The Problem of the Weir.* By J. H. C. SEARLE, B.Sc., Assistant Lecturer in Mathematics in the Victoria University, Manchester †.

§ 1. **T**HE problem of determining the motion of a stream flowing in a horizontal channel, whose bed is subject to slight inequalities of level, was investigated by Lord Kelvin ‡, who assumed the flow to be irrotational, and obtained an approximate solution of the motion. Wien §,

* Lenard and Ramsauer suggest that the light splits up the chlorine molecule into its two neutral atoms.

† Communicated by Prof. Horace Lamb, F.R.S.

‡ Phil. Mag. [5] vol. xxii. p. 353 *et seq.*

§ Wien, *Hydrodynamik*, p. 201.

using the same restrictions, discussed the case in which the change of level was abrupt.

When the fall of the stream-bed is not small compared with the general depth of the stream the problem becomes of some practical importance, and a solution of it might throw light on the theory of the construction of weirs and aqueducts. Although the problem is dealt with in various text-books on Hydraulics*, the treatment is usually somewhat empirical. It seems, therefore, worth while to inquire what information on the subject can be gained from the ordinary hydrodynamical equations when viscosity is neglected. It is true that in the absence of viscosity the problem is indeterminate, but an attempt may be made to represent approximately the physical conditions by assuming a laminar motion of the fluid.

In the present note the motion is supposed to be two-dimensional and steady. The upper and lower stream-beds are taken horizontal, but the intervening connexion may be of any form consistent with continuous flow without impacts. Along the upper and lower reaches the flow is assumed to be ultimately horizontal†, and it is at these places that the motion is considered. In practice these places will be more or less close to the weir, or sloping part of the bed, according to its form.

Given the height of the weir or difference of level of the upper and lower stream-beds, the depth of the upper stream and the distribution of velocity across a vertical section of it where the flow is horizontal, it is proposed to determine. (1) the depth of the lower stream; (2) the distribution of velocity across a vertical section of it where the flow has again become horizontal; and (3) the total horizontal thrust on the weir face or sloping stream-bed.

It will be seen that the motion is not restricted to be irrotational; on the contrary, the fluid may be given any desired degree of spin. Thus, while the solution in any particular case is only partial, the problem considered is more general than the irrotational case usually dealt with.

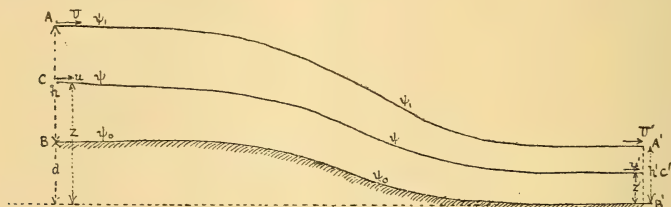
In an Appendix some notes have been added bearing on the work in the paper. As they deal only with the case

* *E. g.*, Bovey, Hydraulics, 1904; Merriman, Hydraulics, 1904.

† The hypothesis of the ultimate horizontality of the lower stream-surface involves, when viscosity is neglected, a distinct assumption. Some remarks in justification are given in §§ 5 and 14. I am indebted to Prof. Lamb for some helpful criticism of this and other points in the paper. Apart from this physical assumption, the results which follow are analytically exact.

where the bed is strictly uniform they have been placed at the end of the work.

§ 2. The figure below represents a vertical section of the stream taken parallel to the banks, the motion being two-dimensional.



z is measured upwards from the bed of the lower stream.

AA' is the free surface (ψ_1);

BB' „ stream-bed (ψ_0);

CC' is any stream-line (ψ);

h is the depth of the upper stream;

d „ total drop of the stream-bed;

U „ surface velocity at A;

u „ velocity at C at a height z .

By accenting these quantities we obtain their values on the lower stream-bed, as shown.

h, d, U , and u (=function of z) are supposed given;

h', U' , and u' are to be found.

Let p be the pressure: then

$$p = f(\psi) - gz - \frac{1}{2}g^2.$$

$$\therefore \text{At A, } \pi = f(\psi_1) - g(h + d) - \frac{1}{2}U^2;$$

$$\text{At A', } \pi = f(\psi_1) - gh' - \frac{1}{2}U'^2.$$

$$\text{Hence, } U'^2 - U^2 = 2g(h + d - h').$$

$$\text{Put } U'/U = \nu, \quad 2gh/U^2 = \kappa, \quad 1 + d/h = \delta, \quad h'/h = \varpi, \quad . \quad (1)$$

$$\therefore \nu^2 - 1 = \kappa(\delta - \varpi). \quad . \quad . \quad . \quad . \quad (2)$$

Here κ and δ are given, while ν and ϖ are unknown.

Let now $\psi + d\psi$ be a stream-line in the neighbourhood of ψ ; and let

$z + dz$ be its height in the upper stream;

$z' + dz'$ be its height in the lower stream.

By the continuity of flow,

$$udz = u'dz' = d\psi.$$

Also, since the vorticity is constant along a stream-line,

$$du/dz = du'/dz'.$$

Hence,

$$du^2/d\psi = du'^2/d\psi,$$

or

$$u^2 = u'^2 + \text{const.}$$

Taking the surface stream-line we find

$$u'^2 = u^2 + U'^2 - U^2, \quad . \quad . \quad . \quad (3)$$

where u and u' are the velocities above and below the weir on the same stream-line.

Substituting this value of u' in $udz = u'dz'$ we have

$$dz' = u dz / (u^2 + U'^2 - U^2)^{\frac{1}{2}}. \quad . \quad . \quad . \quad (4)$$

Put

$$u^2 = U^2 \phi(\zeta), \text{ where } \zeta = (z-d)/h, \text{ and let } \zeta' = z'/h'. \quad (5)$$

From (4)

$$\varpi \zeta' + \text{const.} = \int \left[\frac{\phi(\zeta)}{\phi(\zeta) + \nu^2 - 1} \right]^{\frac{1}{2}} d\zeta.$$

When $z=d$; $z'=0$, *i. e.*, when $\zeta=0$, $\zeta'=0$.

When $z=d+h$, $z'=h'$; *i. e.*, when $\zeta=1$, $\zeta'=1$.

Hence,

$$\varpi = \int_0^1 \left[\frac{\phi(\zeta)}{\phi(\zeta) + \nu^2 - 1} \right]^{\frac{1}{2}} d\zeta.$$

Since, by (2), $\nu^2 - 1 = \kappa(\delta - \varpi)$, we have, finally,

$$\varpi = \int_0^1 \left[\frac{\phi(\zeta)}{\phi(\zeta) + \kappa(\delta - \varpi)} \right]^{\frac{1}{2}} d\zeta. \quad . \quad . \quad . \quad (6)$$

Since u and u' , for physical reasons, have the same sign, it follows that the sign of $\sqrt{(u^2 + U'^2 - U^2)}$ will be the same as that of u . Hence, the positive sign must be attached to the integrand in (6).

When u is given as a function of z , $\phi(\zeta)$ is determined from (5). Equation (6) will then determine ϖ as a function of κ and δ , and thence ν is given by (2). U' and h' are found from (1) and u' is determined from (3), *viz.*,

$$u'^2 = U^2 \{ \phi(\zeta) + \nu^2 - 1 \}.$$

The circumstances of the motion along the lower bed are thus completely found.

§ 3. Equation (6) will, in general, contain a number of radicals after integration, and in the process of rationalizing and simplification, necessary for numerical computation, a number of roots will appear which are irrelevant to the present purpose. After discarding the negative roots there still remains the problem of picking out one from the remainder which will adequately satisfy the physical requirements. Two conditions will suffice to determine this root:—

(1) As the fall of the stream-bed tends to zero the surface-level of the stream must become uniform;

(2) As the velocity of the upper stream tends to zero the surface-level of the whole stream must become uniform.

Expressed analytically these conditions are as follows:—

(1) As $\delta \rightarrow 1$, ϖ must also $\rightarrow 1$;

(2) As $\kappa \rightarrow \infty$, ϖ must $\rightarrow \delta$.

It will now be shown that there is a solution satisfying both these conditions, and that this solution is, in general, unique. In (6) write

$$\varpi = 1 + \eta, \quad \phi/\kappa = \lambda, \quad \delta = 1.$$

Hence,

$$1 + \eta = \int_0^1 \lambda^{\frac{1}{2}} / (\lambda - \eta)^{\frac{1}{2}} d\zeta,$$

or

$$\begin{aligned} \eta &= \int_0^1 \{ \lambda^{\frac{1}{2}} - (\lambda - \eta)^{\frac{1}{2}} \} / (\lambda - \eta)^{\frac{1}{2}} d\zeta \\ &= \eta \int_0^1 d\zeta / (\lambda - \eta)^{\frac{1}{2}} \{ \lambda^{\frac{1}{2}} + (\lambda - \eta)^{\frac{1}{2}} \}. \end{aligned}$$

Hence, $\eta = 0$, *i. e.*, $\varpi = 1$ is a solution when $\delta = 1$.

Also, $\int_0^1 d\zeta / (\lambda - \eta)^{\frac{1}{2}} \{ \lambda^{\frac{1}{2}} + (\lambda - \eta)^{\frac{1}{2}} \} = 1$ is a solution when $\delta = 1$.

A further value $\eta = 0$ will not satisfy the last relation unless

$$\int_0^1 d\zeta / 2\lambda = 1, \text{ i. e., unless } \int_0^1 d\zeta / \phi(\zeta) = U^2 / gh,$$

i. e., unless

$$g \int_0^h dz / u^2 = 1. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Hence, when $\delta = 1$ equation (6) will, in general, furnish one value $\varpi = 1$ (or $\eta = 0$), and one such value only. If, however, the motion is such that (7) is identically satisfied, then $\varpi = 1$ will be a double root of (6) when $\delta = 1$. Assuming

for the present that (7) does not hold, write $\varpi=1+\eta$, $\delta=1+\epsilon$ in (6). The general solution of (6) will then be of the form

$$\eta=f\{\kappa(\epsilon-\eta)\},$$

$$\text{or} \quad \epsilon=\eta+F(\eta)/\kappa, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where $F(\eta)$ is expansible in positive powers of η and does not contain a constant term. The problem of determining η in terms of κ and ϵ may be solved by using Lagrange's theorem*, which gives

$$\eta=\epsilon+\sum_1^{\infty}\frac{(-)^n}{n!\kappa^n}\frac{d^{n-1}}{d\epsilon^{n-1}}\{F(\epsilon)\}^n. \quad . \quad . \quad . \quad (9)\dagger$$

Since $F(\epsilon)$ vanishes with ϵ , therefore (9) makes $\eta\rightarrow 0$ as $\epsilon\rightarrow 0$. It also makes $\eta\rightarrow\hat{\epsilon}$ (i. e., $\varpi\rightarrow\delta$) when $\kappa\rightarrow\infty$. This branch of the function therefore satisfies the two physical conditions mentioned above, and (9) will therefore be taken as the formal solution of the problem.

In order to justify this selection we note that the value $\delta=1$ makes the total fall of the stream-bed zero, and the corresponding value $\varpi=1$ makes the stream-surface level. If some other root of (6) had been chosen, then on making δ tend to unity, ϖ would not have tended also to unity, since relation (7) is not supposed to hold. This would infer the possibility of a standing elevation of some kind, in a uniform horizontal canal, in which the free surfaces on either side of the elevation were at a finite difference of level. The impossibility of this is proved in Appendix (A) for the most general case of non-viscous flow.

If equation (7) be satisfied the above argument breaks down, since there will be two values $\varpi=1$ corresponding to $\delta=1$, and therefore two expansions for η in terms of ϵ corresponding to the two branches of the function (9). It seems probable that the motion is unstable when (7) is true, and is of a different type according as

$$\int_0^1 d\xi/\phi(\xi) \gtrless U^2/gh.$$

A particular case is given in § 5.

§ 4. In the case of a weir it is interesting to determine the resultant horizontal pressure on the face of the weir.

* Whittaker, 'Modern Analysis,' p. 106.

† The series under Σ will contain a term in ϵ if $\int_0^1 d\xi \phi(\xi)$ is convergent, and *vice versa*. In any case $\eta\rightarrow\epsilon$ as $\kappa\rightarrow\infty$.

In the diagram of § 2 consider the mass of fluid bounded by the contour AA'B'BA.

Let P = resultant horizontal pressure on section AB,
 P' = " " " " " " A'B',
 $\mathcal{P}$ = " " " " " " face of weir,
 M = total momentum crossing AB per second,
 M' = " " " " " " A'B' "

Then, rate of change of horizontal momentum of fluid within contour = rate at which horizontal momentum flows in over boundary together with total surface pressure on contour resolved horizontally, since the horizontal body forces vanish.

Hence,

$$0 = \mathcal{P} + P - P' + M - M' - \pi(h + d - h').$$

$$\therefore \mathcal{P} = \pi(h + d - h') + P' - P + M' - M,$$

$$= \pi(h + d - h') + \pi h' + \frac{1}{2}gh'^2 - \pi h - \frac{1}{2}gh^2 + \int_0^{h'} u'^2 dz' - \int_d^{h+d} u^2 dz.$$

But, $u dz = u' dz'$ and $u' = \sqrt{(u^2 + U^2 - U^2)}$.

$$\text{Hence, } \int_0^{h'} u'^2 dz' = \int_d^{h+d} u \sqrt{(u^2 + U^2 - U^2)} dz.$$

$$\therefore \mathcal{P} = \pi d + \frac{1}{2}g(h'^2 - h^2) + \int_d^{h+d} u \{ \sqrt{(u^2 + U^2 - U^2)} - u \} dz. \quad (10)$$

Expressing this in terms of the quantities given in (1) we find

$$\mathcal{P} = \pi d + U^2 h \left[\frac{1}{4} \kappa (\varpi^2 - 1) + \int_0^1 \left[\sqrt{\phi(\zeta) \{ \phi(\zeta) + \kappa(\delta - \varpi) \}} - \phi(\zeta) \right] d\zeta \right]. \quad (11)$$

When ϖ is determined from (5) $\mathcal{P}$ is found from (9).

It will be noticed that

$$\frac{\partial \mathcal{P}}{\partial \varpi} = \frac{1}{2} \kappa U^2 h \left[\varpi - \int_0^1 \left\{ \frac{\phi(\zeta)}{\phi(\zeta) + \kappa(\delta - \varpi)} \right\}^{\frac{1}{2}} d\zeta \right] = 0, \text{ by (5),}$$

as might otherwise be expected.

§ 5. The case of irrotational motion, although probably far removed from Nature, has the prior claim to attention on account of its simplicity and historical interest. In this case we have

$$u = \text{const.} = U.$$

Hence, by (5), $\phi(\zeta) = 1.$

Substituting in (6) we find

$$\varpi = \{1 + \kappa(\delta - \varpi)\}^{-\frac{1}{2}},$$

which after rationalizing gives

$$\kappa\varpi^3 - (1 + \kappa\delta)\varpi^2 + 1 = 0, \quad . \quad . \quad . \quad (12)$$

as a cubic to determine ϖ in terms of κ and δ .

It may be shown that the roots of (12) are given by

$$\varpi = -(\sqrt{3}/2) \cdot (1 + \kappa\delta)^{-\frac{1}{2}} \sec \frac{1}{3}\theta, \quad . \quad . \quad (13)$$

where θ is any value satisfying

$$\cos \theta = (3\sqrt{3}/2) \cdot \kappa(1 + \kappa\delta)^{-3/2}. \quad . \quad . \quad (14)$$

An inspection of (12) will show that the roots are distributed as follows:—

$$-\infty < \varpi_1 < 0 < \varpi_2 < 1 < \delta < \varpi_3 < \delta + 1/\kappa.$$

There are thus two positive roots and one negative root. The last does not appear to have a physical interpretation, but the question arises—which of the two positive roots is to be chosen? If we put $\delta=1$ in (12) there results

$$(\varpi - 1)(\kappa\varpi^2 - \varpi - 1) = 0, \quad . \quad . \quad . \quad (15)$$

of which the only physical solution is $\varpi=1$ *. In accordance with the work of § 3 we write $\delta=1+\epsilon$ and $\varpi=1+\eta$, where ϵ and η are small and vanish together. Substituting in (12) and neglecting squares, &c., of ϵ and η , we have

$$\eta = \kappa\epsilon/(\kappa - 2),$$

so that η is positive or negative according as $\kappa \gtrless 2$.

[The expansion of η in terms of ϵ proceeds as follows:—

$$\begin{aligned} \eta = \frac{\kappa}{\kappa - 2} \epsilon - \frac{3\kappa^2}{(\kappa - 2)^3} \epsilon^2 + \frac{\kappa^3(4\kappa + 10)}{(\kappa - 2)^5} \epsilon^3 - \frac{5\kappa^4(\kappa^2 + 8\kappa + 7)}{(\kappa - 2)^7} \epsilon^4 \\ + \frac{6\kappa^5(\kappa^3 - 3\kappa^2 + 126\kappa - 59)}{(\kappa - 2)^9} \epsilon^5 - \dots \end{aligned}$$

This becomes divergent when $\kappa=2$, i. e., when $U^2=gh$, in accordance with (7) § 3, because when $\kappa=2$, (15) becomes $(\varpi-1)^2(2\varpi+1)=0$, and there is a double root $\varpi=1$. The series is useful for calculation when ϵ is small or when κ is great or small.]

* Appendix A.

Since $\eta \geq 0$ according as $\kappa \geq 2$,
therefore $U' \geq U$ „ „ $U^2 \geq gh$, because $\varpi = h'/h = U/U'$.

Also, $U'^2 - U^2 = 2g(h + d - h')$;
therefore $h' \leq h + d$ according as $U^2 \geq gh$.

Hence, the surface-level of the stream along the lower bed will be higher or lower than the surface-level of the upper stream according as $U^2 \leq gh$.

It will be noticed that the "critical" velocity, $U^2 = gh$, is that of a long wave in a canal of depth h , and it seems probable that when U has this value, or very nearly this value, the motion will become unsteady on account of the tendency of the stream-surface to adjust itself alternately to the higher or lower level, according as U is slightly less than or slightly greater than $(gh)^{1/2}$. Some such effect seems to have been noticed by Bidone in his researches on the flow of water over weirs. From a practical point of view the result may be of use, because it shows that in this type of motion the "critical" velocity should be avoided in order to prevent "scouring" of the channel.

Lord Kelvin*, using a different method, arrived at the approximate formula

$$y = d / (gD/V^2 - 1) ;$$

where y = elevation of surface ($= h + d - h'$ in present notation),

d = „ „ stream-bed (small),

D = a depth lying between h and h' ,

V = a velocity lying between U and U' .

It appears that there is an elevation or depression of the lower stream-surface according as $V^2 \leq gD$ when $d > 0$ and inversely when $d < 0$, *i. e.*, when the stream-bed falls.

In Lord Kelvin's work the values of V and D are necessarily undetermined, although, when the irregularities of the stream-bed are small, we may put approximately the values h and U of the upper stream. The present note shows that the elevation or depression of the lower stream-surface depends *accurately* on the criterion $U^2 \leq gh$, and also does not depend on d being small.

If we reverse the general direction of the stream the theory indicates a depression of the surface when a stream flows from a lower to a higher bed,—a phenomenon often observed in practice †.

* *L. c. ante.*

† Merriman, *Hydraulics*, p. 295.

In the case where the lower stream-surface is depressed ($U^2 > gh$) it may be shown that waves of small amplitude cannot be maintained in the lower stream. For in this case

$$\varpi = 1/\nu < 1 \quad \text{and} \quad U^2/gh > 1.$$

Hence, $U^2/U'^2 \cdot h'/h > g \cdot h'/U'^2,$

i. e., $\varpi/\nu^2 > gh'/U'^2,$

i. e., $\varpi^3 > gh'/U'^2.$

Therefore, $1 > gh'/U'^2,$

or $U'^2 > gh'.$

The velocity of propagation of irrotational waves of small amplitude in a channel of depth h' is V , where

$$V^2 = gh' \cdot \tanh \kappa h' / \kappa h' \quad (\kappa = 2\pi/\text{wave-length}).$$

Hence, V^2 always $< gh'$

i. e., $V \quad \quad \quad < U'.$

Thus, if such waves were ever formed they would be carried away by the preponderating velocity of the lower stream.

§ 6. When $U^2 < gh$ the surface-level of the stream on the lower bed is elevated, but it can be shown that this elevation cannot exceed a certain limit, viz., half the depth of the stream on the upper bed.

For, in this case $\varpi > 1$ and the root chosen lies between δ and $\delta + 1/\kappa$.

Hence, $\delta < \varpi < \delta + 1/\kappa,$

or $1 + d/h < h'/h < 1 + d/h + U^2/2gh.$

Also, in the present case, $U^2 < gh.$

$$\therefore h + d < h' < h + d + h/2,$$

or $0 < h' - (h + d) < h/2.$

Hence, the difference of levels of the upper and lower streams is always less than half the depth of the stream on the upper bed.

§ 7. In the special case where $\kappa = \delta$, *i. e.,* $2gh/U^2 = 1 + d/h$, the cubic (12) admits of a very simple solution. For, in this case, (12) becomes

$$\kappa \varpi^3 - \varpi^2(1 + \kappa^2) + 1 = 0,$$

or $(\kappa \varpi - 1)(\varpi^2 - \kappa \varpi - 1) = 0.$

Hence, when $\kappa < 2$, i. e., $gh < U^2$ or $d < h$, it is easy to derive the following equations:—

$$\varpi = 1/\kappa = 1/\delta, \quad U' = U(1 + d/h), \quad \text{and} \quad h' = h^2/(h + d).$$

When $\kappa > 2$, i. e., $gh > U^2$ or $d > h$, the corresponding values of ϖ , U' , and h' are found from the quadratic $\varpi^2 - \kappa\varpi - 1 = 0$.

§ 8. To calculate the horizontal pressure on the face of the weir put $\phi(\xi) = 1$ in (11). We find

$$\mathcal{P} = \pi d + U^2 h \left\{ \frac{1}{4} \kappa (\varpi^2 + \varpi) - 1 \right\} (\varpi - 1) / \varpi. \quad (16)$$

πd is the atmospheric pressure on the face of the weir and, by means of the inequalities $\varpi \geq 1$ according as $\kappa \geq 2$, it may be shown from (16) that $\mathcal{P}$ always $> \pi d$, so that the pressure is always positive. $\mathcal{P}$ may be found from (16) when ϖ has been determined for any special case from (6).

When $\kappa = \delta$, as in § 7, and $\varpi = 1/\kappa = 1/\delta$, the corresponding pressure may be found at once, viz.,

$$\mathcal{P} = \frac{1}{4} U^2 h (\delta - 1) (3\delta - 1) / \delta = \frac{1}{2} g h^2 d (2h + 3d) / (h + d)^2.$$

§ 9. Turning now to the case where the motion is vortical, let the vorticity of the fluid be everywhere constant. Along both the upper and the lower streams the motion will now be of the “laminar” type given by the ordinary equations when viscosity is retained. Taking the velocity to be zero along the upper stream-bed so as to correspond as nearly as possible to the actual physical conditions, we have

$$u = U \cdot (z - d) / h = U \xi.$$

Hence, by (5), $\phi(\xi) = \xi^2$, and from (6), after integration,

$$\varpi = \{ 1 + \kappa (\delta - \varpi)^{\frac{1}{2}} - \{ \kappa (\delta - \varpi) \}^{\frac{1}{2}} \}, \quad (17)$$

$$\text{from which} \quad \varpi^4 + 4\kappa\varpi^3 - 2\varpi^2(1 + 2\kappa\delta) + 1 = 0. \quad (18)$$

The roots of (18) are distributed as follows:—

$$-\infty < \varpi_1 < -1 < \varpi_2 < 0 < \varpi_3 < 1 < \varpi_4 < \delta.$$

When $\delta = 1$ (18) becomes

$$(\varpi - 1) \{ \varpi^3 + (1 + 4\kappa)\varpi^2 - \varpi - 1 \} = 0,$$

of which the physical solution required is $\varpi = 1$ *. There will not be a second value $\varpi = 1$ unless $\kappa = 0$.

* Appendix A.

Putting $\varpi=1+\eta$, $\delta=1+\epsilon$ in (18) we find to the first order $\eta=\epsilon$, so that $\varpi > 1$. The root chosen is, therefore, such that

$$1 < \varpi < \delta.$$

[In this case (17) leads to the equation

$$\epsilon = \eta + \left(1 + \eta - \frac{1}{1+\eta}\right)^2 / 4\kappa;$$

whence, by (a),

$$\eta = \epsilon - \frac{\epsilon^2}{\kappa} + 4\epsilon^3 \left(\frac{1}{4\kappa} + \frac{1}{2\kappa^2} \right) - 5\epsilon^4 \left(\frac{1}{4\kappa} + \frac{1}{\kappa^2} + \frac{1}{\kappa^3} \right) + 6\epsilon^5 \left(\frac{1}{4\kappa} + \frac{7}{4\kappa^2} + \frac{7}{2\kappa^3} + \frac{7}{3\kappa^4} \right) - 7\epsilon^6 \left(\frac{1}{4\kappa} + \frac{11}{4\kappa^2} + \frac{9}{\kappa^3} + \frac{12}{\kappa^4} + \frac{6}{\kappa^5} \right) + \dots]$$

From (18) ϖ may be expressed as follows:—

$$\varpi = \kappa(\mu-1) + \left\{ \kappa^2(\mu-1)^2 - \sqrt{\left(\frac{\mu-1}{\mu+1} \right)} \right\}^{\frac{1}{2}};$$

where $\mu^2 = \lambda^2/(\lambda^2-1)$ and λ is that root of the cubic $(\lambda^2-1)(\lambda-2\kappa\delta-1) = 2\kappa^2$ lying between 1 and ∞ .

When ϖ has been found from (18) ν is most easily calculated from the equation

$$2\nu = \varpi + 1/\varpi,$$

whence ν always ≥ 1 .

Since

$$1 < \varpi < \delta,$$

therefore

$$1 < h'/h < 1 + d/h,$$

or

$$h < h' < h + d.$$

Hence, although the lower stream is always deeper than the upper, the stream-surface is always depressed on passing from the upper to the lower reaches.

§ 10. The calculation of the pressure on the weir face for this type of motion is effected by putting $\phi(\zeta) = \zeta^2$ in (11). We find

$$\mathcal{P} = \pi d + U^2 h \left[\frac{1}{4} \kappa (\varpi^2 - 1) + \frac{1}{3} \{ 1 + \kappa (\delta - \varpi) \}^{3/2} - \frac{1}{3} \{ \kappa (\delta - \varpi) \}^{3/2} - \frac{1}{3} \right], \quad \dots \quad (19)$$

which may be rationalized by (17) if necessary.

Since, in this type of motion, $\varpi > 1$ and since $(1+x)^{3/2}$ is always greater than $1+x^{3/2}$, (19) shows that $\mathcal{P}$ is always $> \pi d$.

When U , h , and d are given κ and δ are found from (1) and, thence, ϖ may be determined from (17) or (18). This value when substituted in (19) will give the corresponding horizontal pressure on the weir face or sloping bed.

§ 11. Amongst engineers a formula of the "parabolic" type has been proposed as representing the distribution of velocity across a vertical section of a uniform canal. Thus, the equation $u = \alpha + \beta z + \gamma z^2$, in which α is zero or very small, would represent a type of motion in which the velocity is zero, or very nearly so, along the bed of the canal and increased upwards. Experience seemed to show that the velocity was a maximum not at the surface but at some point below it not greater than one fourth the stream depth*.

The adoption of the above formula in the present note would lead to some very unwieldy analysis, and it is therefore proposed to substitute the formula

$$u = U \sin \left\{ \frac{1}{2} \pi (z - d) / h \right\},$$

which makes the velocity zero along the upper stream-bed and a maximum at its surface. Hence,

$$u = U \sin \frac{1}{2} \pi \zeta, \quad \text{or by (5),} \quad \phi(\zeta) = \sin^2 \frac{\pi}{2} \zeta.$$

Substituting in (6) and integrating we find, after some reductions,

$$\{1 + \kappa(\delta - \varpi)\} \sin^2 \frac{1}{2} \pi \varpi = 1. \quad . \quad . \quad (20)$$

[Writing $\varpi = 1 + \eta$ and $\delta = 1 + \epsilon$, (20) may be transformed into

$$\epsilon = \eta + \frac{1}{\kappa} \tan^2 \frac{1}{2} \pi \eta.$$

Using (9), we have

$$\begin{aligned} \eta = \epsilon - \frac{\lambda^2}{\kappa} \epsilon^2 + \frac{2\lambda^4}{\kappa^2} \epsilon^3 - \left(\frac{5\lambda^6}{\kappa^3} + \frac{2\lambda^4}{3\kappa} \right) \epsilon^4 + \left(14 \frac{\lambda^8}{\kappa^4} + 4 \frac{\lambda^6}{\kappa^2} \right) \epsilon^5 \\ - \left(42 \frac{\lambda^{10}}{\kappa^5} + \frac{56}{3} \frac{\lambda^8}{\kappa^3} + \frac{17}{45} \frac{\lambda^6}{\kappa} \right) \epsilon^6 + \dots, \end{aligned}$$

where $\lambda = \pi/2$. It may be more advantageous, however, to expand in terms of $\tan \frac{1}{2} \pi \epsilon$.]

It may be verified that the root required is such that

$$1 < \varpi < \delta.$$

* Bevey, *l. c. ante*, p. 220. When the stream width is small compared with its depth the point of maximum velocity may be lower than stated above.

Hence, $h < h' < h + d$;

so that the stream-surface is always depressed on passing from the upper to the lower regions, but the lower stream is deeper than the upper.

§ 12. Putting $\phi(\zeta) = \sin^2 \frac{\pi}{2} \zeta$ in (11) the pressure $\mathcal{P}$ may be found:

$$\mathcal{P} = \pi d + U^2 h \left[\frac{1}{4} \kappa (\varpi^2 - 1) + \frac{1}{\pi} \left\{ \nu^2 \sin^{-1}(1/\nu) + (\nu^2 - 1)^{\frac{1}{2}} \right\} - \frac{1}{2} \right],$$

where $\nu^2 = 1 + \kappa(\delta - \varpi)$.

Thus $\mathcal{P}$ can be determined for any particular values of U , h , and d , when ϖ has been found for that case from (20).

§ 13. The following Table (p. 786) of values of ϖ , ν , and $\mathcal{P}/U^2 h$ has been calculated for various values of κ and δ in order to institute a comparison between the three types of motion which have been worked out.

From the Table it appears that irrotational motion differs in character from the cases of rotational motion considered. In the former case the depth of the lower stream decreases as the height of the weir increases, κ being kept constant, while in rotational motion the reverse is the case. It follows that calculations based on the assumption of irrotational flow will differ widely in this respect from those based on the more physical assumption of rotational flow.

As a particular case, illustrating the use of the Table, consider a stream whose depth in the upper reaches is 4 ft. Let the height of the weir be 1 ft. and the surface velocity of the upper stream 16 ft. per sec. These values give

$$\delta = 1 + d/h = 1.25, \quad \kappa = 2gh/U^2 = 1.$$

From column I. we find $\varpi = .8431$, $\nu = 1.1861$, $\mathcal{P}/U^2 h = .1138$,

„ „ II. „ $\varpi = 1.2125$, $\nu = 1.0186$, $\mathcal{P}/U^2 h = .1344$,

„ „ III. „ $\varpi = 1.1721$, $\nu = 1.0383$, $\mathcal{P}/U^2 h = .1280$.

Hence, for

Case I. $h' = 3.3724$ ft., $U' = 18.978$ f.p.s., $\mathcal{P} = 116.53$ lb. wt.

„ II. $h' = 4.8500$ ft., $U' = 16.298$ f.p.s., $\mathcal{P} = 137.63$ lb. wt.

„ III. $h' = 4.6884$ ft., $U' = 16.614$ f.p.s., $\mathcal{P} = 131.07$ lb. wt.

Here h' is the depth of the lower stream, U' its surface-velocity, and $\mathcal{P}$ the horizontal pressure on the weir per foot breadth. If the water were at rest with its surface 4 ft.

Phil. Mag. S. 6. Vol. 23. No. 137. May 1912. 3 F

κ		I.					II.				III.			
		1.25	1.50	1.75	2.00		1.25	1.50	1.75	2.00	1.25	1.50	1.75	2.00
.5	δ													
	α	.9261	.8725	.8272	.7893		1.1893	1.3315	1.4551	1.5677	1.1440	1.2257	1.2858	1.3333
	ν	1.0798	1.1461	1.2089	1.2670		1.0148	1.0412	1.0711	1.1027	1.0262	1.0663	1.1100	1.1547
	$\mathcal{P}/U^2h$...	.0620	.1163	.1694	.2199		.0653	.1315	.1971	.2624	.0630	.1208	.1742	.2255
1.0	α	.8431	.7573	.6982	.6527		1.2125	1.3884	1.5471	1.6948	1.1721	1.2795	1.3567	1.4165
	ν	1.1861	1.3204	1.4322	1.5320		1.0186	1.0344	1.0967	1.1424	1.0383	1.1047	1.1804	1.2584
	$\mathcal{P}/U^2h$...	.1128	.2138	.3041	.3885		.1344	.2767	.4244	.6260	.1280	.2488	.3579	.4577
1.5	α	.7590	.6667	.6072	.5629		1.2228	1.4160	1.5928	1.7621	1.1882	1.3113	1.3994	1.4651
	ν	1.3176	1.5000	1.6474	1.7764		1.0203	1.0611	1.1103	1.1648	1.0453	1.1371	1.2353	1.3425
	$\mathcal{P}/U^2h$...	.1586	.2917	.4107	.5202		.2037	.4271	.6627	.9119	.1947	.3845	.5481	.6974
2.0	α	.6852	.5969	.5410	.5000		1.2285	1.4326	1.6232	1.8045	1.1982	1.3333	1.4297	1.5000
	ν	1.4594	1.6753	1.8486	2.0000		1.0212	1.0653	1.1196	1.1792	1.0505	1.1548	1.2808	1.4142
	$\mathcal{P}/U^2h$...	.1942	.3534	.4949	.6250		.2736	.5794	.8984	1.2604	.2622	.5173	.7449	.9433

Column I.—The irrotational case, $u = \text{constant} = U$.
 „ II.—The case of constant vorticity, $u = U(z-d)/h$.
 Column III.—The case in which $u = U \sin \left\{ \frac{\pi}{2} (z-d)/h \right\}$.

above the upper stream-bed, or 5 ft. above the lower stream-bed, the hydrostatic pressure would be about 280 lb. wt. per foot breadth of weir. The effect of the high stream velocity chosen is to reduce the pressure on the weir to about one half of its static value.

Using the same values of U , h , and d , the following are the stream velocities along the lower bed:—18.978, 3.1232, and 4.4768 ft. per sec. respectively. It appears, therefore, that the case II. realizes most nearly the condition of no slipping along the lower boundary of the stream.

§ 14. *Conclusion.*

The obstruction over which the water flows has been alluded to, for shortness, as a weir, but the exact form which this should take, in order to secure the conditions essential to the theory, is not clear. If the flow over the fall be free from turbulence or discontinuity of any kind the results worked out may serve as rough approximations to what is taking place. They would apply more closely, probably, to the case of a stream flowing over a bed whose slope is everywhere gentle. In the latter case Lord Kelvin has stated that corrugations will not appear on the down-stream surface, and the fundamental hypothesis of § 1 will, therefore, be vindicated. In any case the rapidity with which a uniform régime is usually established on passing down-stream from the fall is somewhat remarkable, considering the smallness of viscosity.

The question of the stability of the various types of motion worked out has been left quite untouched, as the method is evidently unsuitable for its discussion. The results may, however, help to assign maximum or minimum limits to the various quantities involved, and may also serve to indicate some of the difficulties which might be encountered in any attempt at a more complete solution.

APPENDIX A.

It has been stated that in a uniform horizontal canal of rectangular cross-section it is possible for a standing finite elevation of the stream-surface to be permanently maintained when the depths and velocities of the stream on either side of the elevation take up suitable values. The impossibility of this has been virtually implied in the preceding work, and the proof now given covers the most general case of non-viscous motion.

Equation (6) of § 2, which was deduced from the condition of "continuity" of flow and the condition that the pressure over the free surface is constant, takes the following form in the present case, viz.,

$$\varpi = \int_0^1 \left[\frac{\phi(\zeta)}{\phi(\zeta) + \kappa(1-\varpi)} \right]^{\frac{1}{2}} d\zeta, \quad . \quad . \quad . \quad (\alpha)$$

for the fall of the stream-bed, d , is now zero, and therefore $\delta = 1 + d/h = 1$.

Again, the horizontal pressure on the weir-face must vanish when there is no weir. Hence, neglecting atmospheric pressure, we have from (11), putting $\delta = 1$,

$$\frac{1}{4}\kappa(\varpi^2 - 1) + \int_0^1 [\sqrt{\phi(\zeta)\{\phi(\zeta) + \kappa(1-\varpi)\}} - \phi(\zeta)] d\zeta = 0. \quad (\beta)$$

(α) and (β) have to be simultaneously satisfied by some value of ϖ . They are both satisfied by the value $\varpi = 1$, i. e., $h = h'$, which corresponds to a uniform flow with an unbroken level surface. We have to show that no other solution is possible.

Put $\lambda(\zeta) = \phi(\zeta)/\kappa$ and $1 - \varpi = \sigma$. In terms of physical constants these are $\lambda(\zeta) = u^2/U^2$, $U^2/2gh = u^2/2gh$ and $\sigma = 1 - h'/h$; where u is the velocity of the "upper" stream at a "distance" $\zeta (= z/h)$ above the lower stream-bed.

(α) and (β) now become

$$1 - \sigma = \int_0^1 \left(\frac{\lambda}{\lambda + \sigma} \right)^{\frac{1}{2}} d\zeta, \quad . \quad . \quad . \quad (\gamma)$$

and

$$\frac{1}{4}\sigma(\sigma - 2) + \int_0^1 \{ \sqrt{\lambda(\lambda + \sigma)} - \lambda \} d\zeta = 0. \quad . \quad . \quad (\delta)$$

(γ) is now satisfied by the value $\sigma = 0$, and (δ) is satisfied by $\sigma^2 = 0$. Before proceeding further these factors will be removed from the respective equations. From (γ)

$$\begin{aligned} \sigma &= \int_0^1 \left\{ 1 - \left(\frac{\lambda}{\lambda + \sigma} \right)^{\frac{1}{2}} \right\} d\zeta \\ &= \int_0^1 \frac{(\lambda + \sigma)^{\frac{1}{2}} - \lambda^{\frac{1}{2}}}{(\lambda + \sigma)^{\frac{1}{2}}} d\zeta \\ &= \int_0^1 \frac{\sigma d\zeta}{(\lambda + \sigma)^{\frac{1}{2}} \{ (\lambda + \sigma)^{\frac{1}{2}} + \lambda^{\frac{1}{2}} \}}. \end{aligned}$$

Hence,

$$\int_0^1 \frac{d\zeta}{(\lambda + \sigma)^{\frac{1}{2}} \{(\lambda + \sigma)^{\frac{1}{2}} + \lambda^{\frac{1}{2}}\}} = 1. \quad . \quad . \quad . \quad (\epsilon)$$

Proceeding in the same manner with (δ) we find

$$\int_0^1 \frac{d\zeta}{\{(\lambda + \sigma)^{\frac{1}{2}} + \lambda^{\frac{1}{2}}\}^2} = \frac{1}{2}. \quad . \quad . \quad . \quad . \quad (\eta)$$

It now remains to be shown that (ϵ) and (η) are not satisfied simultaneously by any value of σ .

$$\text{Put} \quad (\lambda + \sigma)^{\frac{1}{2}} + \lambda^{\frac{1}{2}} = \mathfrak{S}^{\frac{1}{2}},$$

where $\mathfrak{S} \equiv \mathfrak{S}(\zeta, \sigma)$ is a function of both ζ and σ .

$$(\epsilon) \text{ becomes } \int_0^1 \frac{d\zeta / (\mathfrak{S} + \sigma) = \frac{1}{2}}{\left. \begin{array}{l} \text{and } (\eta) \quad \quad \quad \int_0^1 \frac{d\zeta / \mathfrak{S}}{\quad \quad \quad} = \frac{1}{2} \end{array} \right\}. \quad . \quad . \quad . \quad . \quad (\lambda)}$$

$$\text{Now } \lambda^{\frac{1}{2}} = u / (2gh)^{\frac{1}{2}}.$$

$$\begin{aligned} \text{Also, } \lambda + \sigma &= u^2 / 2gh + 1 - h' / h = \{u^2 + 2g(h - h')\} / (2gh), \\ &= (u^2 + U'^2 - U^2) / (2gh), \\ &= u'^2 / (2gh), \text{ by (3).} \end{aligned}$$

$$\therefore (\lambda + \sigma)^{\frac{1}{2}} = u' / (2gh)^{\frac{1}{2}}.$$

For physical reasons, the same sign must be attached to both $\lambda^{\frac{1}{2}}$ and $(\lambda + \sigma)^{\frac{1}{2}}$. Also $\lambda + \sigma$ is always positive: hence,

$$\mathfrak{S} = \lambda + \sigma + 2\lambda^{\frac{1}{2}}(\lambda + \sigma)^{\frac{1}{2}} + \lambda; \therefore \mathfrak{S} > 0.$$

$$\text{Also, } \mathfrak{S} + \sigma = 2[\lambda + \sigma + \lambda^{\frac{1}{2}}(\lambda + \sigma)^{\frac{1}{2}}]; \therefore \mathfrak{S} + \sigma \geq 0.$$

Whether σ be positive or negative the equations (λ) cannot be satisfied by any value of σ , except by a further value $\sigma = 0$, and therefore the only physical solution of the problem is given by $\varpi = 1$ or $h' = h$. We conclude that a permanent standing elevation, where the stream depths are different on either side, cannot be maintained in an open channel of the form contemplated.

APPENDIX B.

It appears that both of the equations last written will be satisfied by a further value $\sigma = 0$, provided

$$\int_0^1 \frac{d\zeta / \mathfrak{S} = \frac{1}{2}}{\quad \quad \quad} \quad . \quad . \quad . \quad . \quad . \quad (\mu)$$

and it is interesting to inquire into the physical meaning of this relation.

q whose components are the four coordinates of a space-point, say

$$q' = aqb, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where in the case of *pure* rotation a and b must of course be either *unit*-quaternions or at least such that $T^2a \cdot T^2b = 1$; T denoting the tensor.

On the other hand, it is widely known that the so-called Lorentz-transformation of the union of ordinary space (x, y, z) and time (t) , which is the basis of the modern theory of Relativity, corresponds precisely to a (hyperbolic) rotation of the four-dimensional manifoldness (x, y, z, t) , or of what Minkowski called the "world."

Hence the obvious idea of representing explicitly the Lorentz-transformation in the quaternionic shape (1),—which, together with some allied questions, will be the subject of the present paper.

To solve this simple problem we have only to write down the well-known relativistic transformation, *i. e.*, the formulæ of Einstein, then to develop the triple product in (1) and to compare the two.

For our purpose it will be most convenient to put Einstein's formulæ at once in vector form, eliminating thus the quite unessential choice of the axes of coordinates. Let the vector $\mathbf{v} = v\mathbf{u}$ denote the uniform velocity of the system $S' (x', y', z', t')$ relatively to the system $S (x, y, z, t)$ *. Let O, O' be a pair of points in S and S' , respectively, which coincide with one another for $t = t' = 0$. Call $\mathbf{r} (= x\mathbf{i} + y\mathbf{j} + z\mathbf{k})$ the vector drawn in S from O as origin, and $\mathbf{r}'$ the corresponding vector in S' , drawn from O' as origin. Then the transformation in question may be stated as follows:—The component of $\mathbf{r}'$ normal to the velocity $\mathbf{v}$ is equal to that of $\mathbf{r}$, *i. e.*

$$\mathbf{r}' - (\mathbf{r}'\mathbf{u})\mathbf{u} = \mathbf{r} - (\mathbf{r}\mathbf{u})\mathbf{u}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (\alpha)$$

whilst the component of $\mathbf{r}'$ taken along the direction of motion is altered according to the formula

$$\mathbf{r}'\mathbf{u} = \gamma[(\mathbf{r}\mathbf{u}) - vt], \quad . \quad . \quad . \quad . \quad . \quad . \quad (\beta)$$

where $\gamma = (1 - \beta^2)^{-1/2}$, $\beta = v/c < 1$, c = velocity of light †.

* $\mathbf{u}$ being a unit-vector in the direction of motion of S' relatively to S and v the absolute magnitude of its velocity.

† In these and in all following formulæ $(\mathbf{r}\mathbf{u})$, generally $(\mathbf{A}\mathbf{B})$, means the modern scalar product of the vectors $\mathbf{A}, \mathbf{B}$, that is to say $AB \cos(\mathbf{A}, \mathbf{B})$; hence $(\mathbf{A}\mathbf{B})$ is the *negative* scalar part of the complete Hamiltonian product, $\mathbf{A}\mathbf{B}$:

$$(\mathbf{A}\mathbf{B}) = -\mathbf{SAB}.$$

On the other hand, the modern vector product $\mathbf{VAB}$ is *identical* with Hamilton's $\mathbf{VAB}$.

Finally, the time is transformed according to

$$t' = \gamma \left[t - \frac{1}{c^2} (\mathbf{r} \mathbf{v}) \right].$$

To get the resultant $\mathbf{r}'$ take the sum of (α) and of $(\beta) \times \mathbf{u}$. Then write, for the sake of subsequent convenience,

$$l = \iota c t, \quad \iota = \sqrt{-1},$$

and similarly $l' = \iota c t'$.

Thus, the relativistic formulæ will become

$$\left. \begin{aligned} \mathbf{r}' &= \mathbf{r} + (\gamma - 1) (\mathbf{r} \mathbf{u}) \mathbf{u} + \iota \beta \gamma \mathbf{u} \\ l' &= \gamma [l - \iota \beta (\mathbf{r} \mathbf{u})], \end{aligned} \right\} \dots \dots (2)$$

quite independent of any system of coordinate-axes.

Now, to obtain the required quaternionic representation (1) of the whole transformation (2), let us introduce the quaternion

$$q = \mathbf{r} + l = \mathbf{r} + \iota c t, \dots \dots (3)$$

and similarly $q' = \mathbf{r}' + l' = \mathbf{r}' + \iota c t' \dots \dots (3')$

Then the problem will consist in finding a pair of quaternions a, b such that

$$\mathbf{r}' + l' = a(\mathbf{r} + l)b,$$

and will be solved by developing the right side of this equation.

Having done this, explicitly, and compared with (2), I found immediately that the quaternions a, b can differ from one another only by an ordinary scalar factor, and since this may be distributed equally among a, b (their tensors entering only by the product), we may as well take simply *equal* a, b , say, both = Q . In fact, then, the form (1) is much too general for our purpose. Thus, to spare the reader any superfluous complication, let us at once seek for

$$q' = Q q Q \dots \dots (1a)$$

as the quaternionic equivalent of (2).

Denote the unknown vector and scalar parts of Q by $\mathbf{w}$ and s respectively, *i. e.* write

$$Q = \mathbf{w} + s. \dots \dots (4)$$

Then, developing the complete product of q , Q , by (3) and (4), and by the fundamental rules of Hamilton's Calculus,

$$qQ = V\mathbf{r}\mathbf{w} + l\mathbf{w} + s\mathbf{r} - (\mathbf{r}\mathbf{w}) + sl,$$

and similarly ,

$$\begin{aligned} q' = QqQ &= V\mathbf{w}V\mathbf{r}\mathbf{w} - \mathbf{w}(\mathbf{r}\mathbf{w}) + 2sl\mathbf{w} + s^2\mathbf{r} - 2s(\mathbf{w}\mathbf{r}) + (s^2 - w^2)l \\ &= (w^2 + s^2)\mathbf{r} - 2(\mathbf{r}\mathbf{w})\mathbf{w} + 2sl\mathbf{w} + (s^2 - w^2)l - 2s(\mathbf{r}\mathbf{w}), \end{aligned}$$

whence, splitting into the vector and scalar parts,

$$\left. \begin{aligned} \mathbf{r}' &= (w^2 + s^2)\mathbf{r} - 2(\mathbf{r}\mathbf{w})\mathbf{w} + 2sl\mathbf{w} \\ l' &= (s^2 - w^2)l - 2s(\mathbf{r}\mathbf{w}) \end{aligned} \right\} \dots \dots (5)$$

Comparing this with (2), we get at once, as the conditions to be fulfilled by $\mathbf{w}$, s ,

$$\left. \begin{aligned} w^2 + s^2 &= 1 ; \quad s^2 - w^2 = \gamma ; \quad 2sw = i\beta\gamma \\ \mathbf{w} &= w\mathbf{u}. \end{aligned} \right\} \dots \dots (6)$$

Hence $w = \pm \sqrt{(1 - \gamma)/2}$, $s = \pm \sqrt{(1 + \gamma)/2}$, where, to satisfy the third of the conditions (6), we must take *both* square roots with the upper or both with the lower sign ; therefore

$$Q = \pm (\sqrt{(1 + \gamma)/2} + \mathbf{u}\sqrt{(1 - \gamma)/2}),$$

and since in (1 a) the quaternion Q appears twice, the choice of the $\pm$ sign becomes indifferent.

Thus, we obtain finally the required quaternionic expression of the relativistic transformation

$$\left. \begin{aligned} q' &= QqQ \\ \text{with } Q &= \frac{1}{\sqrt{2}}(\sqrt{1 + \gamma} + \mathbf{u}\sqrt{1 - \gamma}), \end{aligned} \right\} \dots \dots (I.)$$

$\mathbf{u}$ being a unit vector in the direction of motion of S' relatively to S .

Observe that $\gamma = (1 - v^2/c^2)^{-1/2} > 1$, so that the vector of Q is *imaginary*, whilst its scalar is real.

The tensor of Q is 1 ; thus denoting its *angle* by α , i. e., writing

$$Q = \cos \alpha + \mathbf{u} \sin \alpha = e^{a\mathbf{u}}, \dots \dots (7)$$

we have, by (I.),

$$\cos \alpha = \sqrt{(1 + \gamma)/2}, \quad \sin \alpha = \sqrt{(1 - \gamma)/2}.$$

Hence

$$\sin 2\alpha = \sqrt{1-\gamma^2} = \iota\beta\gamma = \frac{\iota\beta}{\sqrt{1-\beta^2}}$$

or

$$2\alpha = \operatorname{arctg}(\iota\beta) = \operatorname{arctg}\left(\iota \frac{v}{c}\right). \quad \dots \dots (8)$$

Now this is precisely the (imaginary) angle of rotation in the plane t, x^* of Minkowski's four-dimensional world, corresponding to the transformation (2). Hence, by (I.) and (7), we may say that one half of this rotation is effected by Q as a prefactor and the other half by the same quaternion as a postfactor †. This circumstance throws a peculiar light on each of our Q 's.

But what we are mainly concerned with is their union, which considered as an operator may be written

$$\omega = Q[\]Q, \quad \dots \dots \dots (I.a)$$

the vacant place being destined for the operand.

We have just seen that this simple operator converts the quaternion $q = \mathbf{r} + \iota ct$ into its relativistic correspondent q' . Our q is equivalent to Minkowski's "space-time-vector of the first kind" or to Sommerfeld's "Vierervektor" x, y, z, l . These authors call by this same name any *such and only such* tetrad of scalars (three real and the fourth imaginary) which transforms in the same way as x, y, z, l ,—adding where it is necessary the emphasizing epithet "Weltvector" ‡.

* The axis of x coinciding with $\mathbf{u}$, and x itself being our $(\mathbf{ru})$.

† At the first sight it might seem that, the axis of Q being $\mathbf{u}$, this quaternion turns $\mathbf{r}$ round $\mathbf{u}$, *i. e.* in the plane y, z normal to $\mathbf{u}$, while in Minkowski's representation the rotation is in the plane x, t . But this is only an apparent contradiction. In fact,

$$Q\mathbf{r} = \cos \alpha \cdot \mathbf{r} + \sin \alpha \cdot \mathbf{V}\mathbf{ur} + \text{scalar},$$

that is to say, Q as a prefactor turns the transversal component of $\mathbf{r}$ round $\mathbf{u}$ by the angle $+\alpha$ and stretches its longitudinal component; similarly Q as a postfactor, besides stretching the longitudinal component of $\mathbf{r}$, turns its transversal component round $\mathbf{u}$ by the angle $-\alpha$, thus undoing the rotatory effect of the prefactor. Hence, what remains in the final result is but a stretching of $\mathbf{r}$'s longitudinal component and a change of l or t , and this amounts precisely to the Minkowskian rotation in the plane x, t .

‡ H. Minkowski, *Die Grundgleichungen für d. elektromagn. Vorgänge in bewegten Körpern*, Götting. Nachrichten, 1908; Raum und Zeit, *Physik. Zeitschrift*, vol. x. (1909),—also separatim. A. Sommerfeld, *Zur Relativitätstheorie*, i. and ii., *Annalen d. Physik*, vol. xxxii., xxxiii. (1910).

See also the admirably clear and beautiful book *Das Relativitätsprinzip* by M. Laue (Braunschweig, 1911), where the whole work of Einstein, Minkowski, and Sommerfeld, together with the author's own contributions, will be found fully developed.

Similarly we could call our q and any covariant quaternion a "world-quaternion"; but possibly the less pretentious name *physical quaternion* will do as well. Also, at least in the beginning, no further specification of the "kind" is needed.

Thus $\omega = Q[]Q$, defined by (I.), or by (7) and (8), is what I should like to call the relativistic *transformer* of any physical quaternion.

To get the inverse transformer ω^{-1} , viz. that which turns q' into q , apply to both sides of the equation $q' = QqQ$ the inverse quaternion Q^{-1} as a pre- and a postfactor; then, remembering that $Q^{-1}Q = QQ^{-1} = 1$, the result will be

$$q = Q^{-1}q'Q^{-1},$$

or $\omega^{-1} = Q^{-1}[]Q^{-1},$

and since Q is a unit quaternion, its inverse is also its conjugate, *i. e.* Hamilton's KQ , which may be more conveniently written Q_c ; hence

$$\omega^{-1} = Q_c [] Q_c, \quad . \quad . \quad . \quad . \quad . \quad . \quad (I.b)$$

where $Q_c = \cos \alpha - \mathbf{u} \sin \alpha$. Thus, we see that the inverse transformer is got from the direct simply by changing the sign of the angle α or by inverting the direction of $\mathbf{u}$,—as it must be.

Observe that, since the product of quaternions is distributive, the transformer ω has also the *distributive* property, *i. e.*, A, B being any quaternions*,

$$Q[A + B]Q = QAQ + QBQ, \quad . \quad . \quad . \quad . \quad (9)$$

and consequently, if ∂ be any scalar differentiator, also

$$Q[\partial A]Q = \partial QAQ,$$

since Q , being constant, is not exposed to ∂ 's action. Again, by the *associative* property of quaternionic products, the dot signifying a separator,

$$A \cdot QBQ = AQ \cdot BQ,$$

and so on. For our present purpose we scarcely need a full enumeration of ω 's properties.

* *I. e.* generally complete quaternions but also, more especially, pure scalars or pure vectors, either simple- or bi-vectors, that is to say real or complex. The **heavy type** (and this merely to suit the general custom) shall be henceforth used only for *pure vectors*, both real and complex.

In the above we have been concerned with q as an example, or in fact the very prototype, of a physical quaternion. Another example, which will be needed in the sequel, is the quaternionic equivalent of Sommerfeld's "Viererdichte," or Laue's "Viererstrom," say

$$C = \rho \left(\epsilon + \frac{1}{c} \mathbf{p} \right), \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

which we may accordingly call the *current-quaternion*. Here ρ means the volume-density of electricity and $\mathbf{p}$ the velocity of its motion relatively to the system S . To prove that C is a *physical quaternion*, write $\mathbf{p} = d\mathbf{r}/dt$, and consequently

$$C = \epsilon \rho \frac{dq}{dl}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (10a)$$

and notice that, the charges of corresponding volumes in S and S' being equal (by a fundamental postulate), dl/ρ is itself an invariant of the Lorentz-transformation.

The transformer (I. a) may, of course, be applied not only to quaternionic magnitudes, but also to operators, as, for example, to differentiators, which have the structure of a quaternion. If Ω be an operator of this kind, in the system S , and Ω' its relativistic correspondent in S' , and if $\Omega' = Q\Omega Q$, we shall say that the operator Ω has the *character* of a physical quaternion.

As a chief example of such an operator, which also will be needed for what follows, we shall consider here our quaternionic equivalent of Minkowski's matrix called by him "lor" to the honour of Lorentz. This will simply be the Hamiltonian ∇ plus the scalar differentiator $\partial/\partial l$. Let us denote it by D ,

$$D = \frac{\partial}{\partial l} + \nabla. \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$= \partial/\partial l + i\partial/\partial x + j\partial/\partial y + k\partial/\partial z.$$

Comparing this with

$$q = l + \mathbf{r} = l + ix + jy + kz,$$

we see at once that the operator D will transform precisely as q did, *i. e.*

$$D' = QDQ. \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Thus D has the character of a physical quaternion.

To obtain the above representation of the relativistic formulæ (2) we have introduced the quaternion $q=l+r$. Now, for this purpose we might as well have used its conjugate, *i. e.*,

$$q_c=l-r, \dots \dots \dots (3a)$$

and the corresponding $q'_c=l'-r'^*$. It may often be convenient to recur to q_c and it is therefore of some interest to know how it transforms. Now, a glance at (2) suffices to see that both of these formulæ remain unchanged if, having changed the signs of r, r' (and leaving l, l' as before), we change also the sign of u . Thus it is seen that

$$q'_c=Q_c q_c Q_c, \text{ say } =\omega_c q_c \dots \dots \dots (I.c)$$

where $Q_c=\cos \alpha -u \sin \alpha =e^{-\alpha u}.$

Now q_c has precisely the same office as q , that is to say, (I.) and (I.c) are but two expressions of one and the same thing, namely, of the Lorentz-transformation. Hence q_c and any quaternion covariant with q_c is certainly a physical quaternion as well as q and its covariants.

Thus, *the conjugate of a physical quaternion will again be a physical quaternion.* If the original transformed as q , its conjugate will transform as q_c . If A is covariant with q , then A_c is covariant with q_c , and *vice versa*. Speaking of a physical quaternion we shall, when necessary, add the explanation *cov. q* or *cov. q_c*. But generally, for the sake of shortness, this will be omitted, and any letters, as A, B, a, b , &c., *without the subscript c* will be used to denote quaternions *covariant with q*. Observe that, with the above (formal) extension of our original definition, two physical quaternions may be either covariant with one another or not; in the last case we may call them *antivariant*, one being *cov. q*, and the other *cov. q_c*. Thus, by the above convention, A, B_c or a, b_c will denote pairs of antivariant quaternions, the first in each pair transforming as q , and the second as q_c .

The above transformer $\omega_c=Q_c[]Q_c$, which by (I.b) becomes simply identical with ω^{-1} , is, of course, distributive, quite in the same way as $\omega=Q[]Q$. Thus the *sum*, or difference, of two *mutually covariant* (but not of antivariant) physical quaternions will again be a physical quaternion.

* It can be proved immediately that $(q_c)'=(q')_c$. Therefore both may be written simply q'_c .

Notice also that the invariance of q 's tensor, $Tq'=Tq$, which follows immediately from (I.) (since Q is a unit quaternion), may be written :

$$q'q'_c=qq_c.$$

The *reciprocal* of a physical quaternion is also a physical quaternion. For we have

$$a^{-1} = a_c(Ta)^{-2},$$

while the tensor Ta of a physical quaternion is already known to be an invariant. Notice that a and a^{-1} are mutually antivariant.

Now for the *product* of physical quaternions. Take any pair a, b of such quaternions. Leave aside a, b which transforms in the unmanageable way $a'b' = QaQ^2bQ$ (a, b being torn asunder), and pass at once to the product of antivariant factors, which might perhaps be called the *alternating product*, say

$$L = a_c b. \quad (13)$$

Then $L' = Q_c a_c Q_c \cdot Q b Q$, whence by the associative property, and remembering that $Q_c Q = 1$,

$$L' = Q_c L Q. \quad (13')$$

Thus, L is certainly not a physical quaternion of the kind already considered; but since it is transformed in such a simple way and since it has, as will be seen in the sequel, an almost immediate bearing upon relativistic Electromagnetism, it deserves to be considered a little more fully. Consider, then, the conjugate of L . Remember the elementary rule, by which the conjugate of the product of any number of quaternions is the product of their conjugates in the *reversed* order, *i. e.* in our case

$$L_c = b_c a. \quad (14)$$

Now, transforming this, we get in quite the same way as above

$$L'_c = Q_c L_c Q. \quad (14')$$

Hence we see that $Q_c [] Q$ (II.)

is the relativistic transformer of *both* $L = a_c b$ and its conjugate L_c . Similarly,

$$Q [] Q_c. \quad (II. a)$$

will be the transformer of *both* $R = ab_c$ and its conjugate $R_c = ba_c$. Thus the behaviour of L and R is characteristically distinct from that of q or of q_c .

Without trying as yet to invent for these kinds of quaternions any particular names, let us provisionally call any

quaternion which is transformed by (II.) or by (II. a) an *L-quaternion* and an *R-quaternion*, respectively*.

Now, $Q_c[]Q$, being the transformer of *both* L and L_c , is also the transformer of their sum and of their difference, i. e. also of the *scalar* and of the *vector parts* of the quaternion L separately, say $s=SL$ and $A=VL$. Now, s being a scalar, we have

$$s' = Q_c s Q = s Q_c Q = s,$$

i. e. s is an invariant. Then

$$A' = Q_c A Q,$$

and since Q, Q_c are unit quaternions, the tensor of A is another invariant.

Thus, the scalar of any *L-quaternion* and the tensor of its vector are invariants, while the vector itself is transformed into

$$VL' = Q_c[VL]Q. \quad . \quad . \quad . \quad . \quad (III.)$$

Or use the form $L = \sigma(\cos \epsilon + a \sin \epsilon)$, where a is the unit of A . Then $\sigma \cos \epsilon$ and $\sigma \sin \epsilon$ are invariants and consequently also σ and ϵ , so that another form of the last theorem will be :—

The tensor and the angle (or argument) of any *L-quaternion* are invariants, while its axis is transformed by $Q_c[]Q$.

In quite the same way it will be seen that SR is invariant and

$$VR' = Q[VR]Q_c, \quad . \quad . \quad . \quad . \quad (III. a)$$

or in other words :—

The tensor and the angle of any *R-quaternion* are invariants, while its axis is transformed by $Q[]Q_c$.

If we wish to return to the generating factors a_c &c., we can write the above properties :

$$Sa_c'b' = Sa_cb. \quad . \quad . \quad . \quad . \quad (15)$$

$$Va_c'b' = Q_c[Va_cb]Q, \quad . \quad . \quad . \quad . \quad (16)$$

and similarly

$$Sa'b_c' = Sab_c. \quad . \quad . \quad . \quad . \quad (15 a)$$

$$Va'b_c' = Q[Vab_c]Q_c. \quad . \quad . \quad . \quad . \quad (16 a)$$

But as a rule it is better to avoid any splitting of quaternions, if we are to expect simplicity and other advantages from the use of quaternionic language.

* L, R , being initials of *left, right*, may remind us of the position of that of the two generating factors which (as a_c or b_c) has the subscript c , i. e. which is cov. q_c .

or the transformer of $\mathbf{Y}$ is $Q[\]Q_0$. Here the meaning of D_0 is of course, according to (11),

$$D = \frac{\partial}{\partial t} - \nabla. \quad (11')$$

Notice that $\mathbf{X}$ and $\mathbf{Y}$ may be but are not necessarily full quaternions*; they can be, for example, pure vectors, either real (or ordinary vectors) or complex, i. e. *bivectors*, if we are to retain Hamilton's terminology.

Let us now pass to consider the fundamental electromagnetic equations "for the vacuum," as they are recently called, i. e. the system of differential equations

$$\left. \begin{aligned} \frac{\partial \mathbf{E}}{\partial t} + \rho \mathbf{p} &= c. \text{curl } \mathbf{M}, \quad \text{div } \mathbf{E} = \rho \\ \frac{\partial \mathbf{M}}{\partial t} &= -c. \text{curl } \mathbf{E}, \quad \text{div } \mathbf{M} = 0 \end{aligned} \right\}, \quad (18)$$

where $\mathbf{E}$, $\mathbf{M}$ are the electric and magnetic vectors of the field, respectively, ρ the volume-density of electricity and $\mathbf{p}$ the vectorial velocity of its motion, both ρ and $\mathbf{p}$ being given functions of space and time.

First, to condense these equations, put together the electric and the magnetic vectors to make up the *electromagnetic bivector* (or the bivector of the field)

$$\mathbf{F} = \mathbf{M} - i\mathbf{E} \quad (19)$$

and write again $l = ict$. Both *curl* and *div* being distributive, this will give us instead of the four vector equations (18) the two bivectorial equations †

$$\frac{\partial \mathbf{F}}{\partial t} + \text{curl } \mathbf{F} = \frac{1}{c} \rho \mathbf{p}; \quad \text{div } \mathbf{F} = -i\rho,$$

or, using Hamilton's symbols,

$$\frac{\partial \mathbf{F}}{\partial t} + \mathbf{V} \nabla \mathbf{F} = \frac{1}{c} \rho \mathbf{p}; \quad \mathbf{S} \nabla \mathbf{F} = i\rho.$$

* This has no influence on their transformational peculiarities as expressed in the above quaternionic form.

† The reader will find these equations together with the corresponding bivectorial form of the density of energy and the Poynting flux in my paper published in 1907 in the *Annalen der Physik*, vol. xxii., and (supplement) vol. xxiv. I was then unaware of their possible application to the present purpose. (The η of that paper is the above $i\mathbf{F}$.)

Now, remembering that $V\nabla\mathbf{F} + S\nabla\mathbf{F} = \nabla\mathbf{F}$ and using the quaternionic differentiator D , explained by (11), the last two coalesce at once into the single equation

$$D\mathbf{F} = C, \quad . \quad . \quad . \quad . \quad . \quad (VI.)$$

in which C is the current-quaternion, as defined by (10).

Thus, *the whole system of four equations* (18), the fundamental equations of the electron theory, are represented by *one* quaternionic equation, (VI.).

This condensation is even more complete than in Minkowski's matrix-form, which consists of *two* equations, *lor* $f = -s$, *lor* $f^* = 0$ (loc. cit., § 12), one for the first pair of (18) and the other for the second pair, or in Sommerfeld's equivalent four-dimensional vector form: $\text{Div } f = P$ and $\text{Div } f^* = 0$ (loc. cit., § 5). Here P is the "Vierervektor" corresponding to the current-quaternion C , and f the "Sechservektor" corresponding to the bivector $\mathbf{F}$, while f^* is the "supplement" (Ergänzung) of f , which is another "Sechservektor," though very nearly related to f . Minkowski's f is an alternating matrix of 4×4 elements. But let us return to our quaternionic differential equation (VI.).

C is a (given) physical quaternion cov. q. The operator D has also the structure of q . What is the relativistic transformer of $\mathbf{F}$? By (V.) we see at once that it is

$$Q_c[]Q,$$

or that $\mathbf{F}$ is transformed like a (scalarless) *L-quaternion*. Thus, the answer is already contained in (V.). But to see clearly the true meaning of the process implied in the relativistic transformation, let us repeat again the whole reasoning somewhat more explicitly. We have, in the system S , as an expression of the laws of electromagnetic phenomena, the equation

$$D\mathbf{F} = C. \quad . \quad . \quad . \quad . \quad . \quad (S)$$

Now, what the Principle of Relativity requires is the same form of the law in the system S' , i. e.

$$D'\mathbf{F}' = C'. \quad . \quad . \quad . \quad . \quad . \quad (S')$$

Suppose also that both of these equations have been fully confirmed by experience. How are $\mathbf{F}'$ and $\mathbf{F}$ correlated? To adopt language adapted to the general case, use in the accented law or equation (S') the transformer already known, *i. e.* in our present case $Q[]Q$ for both D and C ; then it becomes

$$QDQ\mathbf{F}' = QCQ, \text{ or } DQ\mathbf{F}' = CQ,$$

or, by the non-accented equation (S),

$$DQF' = DFQ.$$

Hence, rejecting an additive function of obvious properties, *i. e.* requiring that F' shall vanish together with F ,

$$QF' = FQ,$$

or finally, Q being a unit-quaternion,

$$F' = Q_c F Q, \quad . \quad . \quad . \quad . \quad . \quad (VII.)$$

which is the required correlation, identical with the above *. Henceforth we shall have to admit, in the name of Relativity, bivectors transforming like this calling them, say, *physical bivectors* (or in Minkowski's way, "world"-bivectors). Or we can make the *L-quaternion* (of which F is the vector part) the master, calling it, say, a (*left*) *physical quaternion of the II. kind*, and writing F as its special case

$$F = VL = V_a b. \quad . \quad . \quad . \quad . \quad . \quad (20)$$

(The supplementary scalar, $S_a b$, necessary to convert F into a full quaternion, would present no difficulties, since it has been proved to be an invariant.) The short name *physical quaternion* might then continue to stand for *physical quaternion of the first kind*, of which q is the standard.

But leave aside questions of nomenclature and return to (VII.). To verify this short formula remember that, by (I.),

$$Q = \sqrt{(1+\gamma)/2} + u \sqrt{(1-\gamma)/2}, \quad Q_c = \sqrt{(1+\gamma)/2} - u \sqrt{(1-\gamma)/2},$$

and expand the right side of (VII.). Then

$$F' = (1-\gamma)(Fu)u + \gamma F + i\beta\gamma VFu, \quad . \quad . \quad (21)$$

or splitting into the real and imaginary parts and remembering (19),

$$\left. \begin{aligned} E' &= (1-\gamma)(Eu)u + \gamma E + \beta\gamma V_u M \\ M' &= (1-\gamma)(Mu)u + \gamma M - \beta\gamma V_u E \end{aligned} \right\} . \quad . \quad . \quad (21a)$$

* Our quaternionic formula (VII.) resembles entirely Minkowski's

$$f' = A^{-1} f A,$$

in which A is a matrix of 4×4 elements, and A^{-1} its reciprocal; *loc. cit.* § 11. The reason of this analogy will easily be seen to depend on the circumstance that both the product of quaternions and the product of matrices have the *associative property*. But at any rate the multiplication by a quaternion, like Q or Q_c , is actually done in a much more simple way than the application of a matrix of 4×4 elements.

Observe also that the above analogy does not extend to the transformation of Minkowski's vectors of the I. kind and our physical quaternions; in fact, here the matrix-form is

$$s' = sA, \text{ with } s = |s_1, s_2, s_3, s_4|,$$

whereas the quaternionic form is

$$q' = QqQ.$$

where C_c is the conjugate current-quaternion $\rho(\iota - \mathbf{p}/c)$ and D_c the conjugate differential operator $\partial/\partial l - \nabla$, as already explained.

We now see, by (V.a), that $\mathbf{G}$ is transformed like an *R-quaternion*, i. e.

$$\mathbf{G}' = \mathbf{Q}\mathbf{G}\mathbf{Q}_c. \quad \text{. (VII.a)}$$

Again we may write, similarly to (20),_i

$$\mathbf{G} = \mathbf{V}\mathbf{R} = \mathbf{V}d\mathbf{e}_c, \quad \text{. (20a)}$$

d , e_c being a pair of physical quaternions covariant with q and q_c respectively. And since $\mathbf{G}$ is a *physical bivector*, just as much as $\mathbf{F}$, we may again call $\mathbf{R} = d\mathbf{e}_c$ a (*right*) *physical quaternion of the second kind*.

Notice that, at least for the time being, we have no need of both $\mathbf{F}$ and $\mathbf{G}$, since we require either $\mathbf{F}$ only or $\mathbf{G}$ only. (Possibly for the further development of Quaternionic Relativity the simultaneous use of $\mathbf{F}$, $\mathbf{G}$ may turn out to be convenient or even necessary.)

As regards the relation of (20a) to (20), observe that generally we cannot write $d = a$, $e = b$; in fact, the reader will easily prove for himself that this would require $(\mathbf{E}\mathbf{M}) = 0$, i. e. $\mathbf{E} \perp \mathbf{M}$, and would not, consequently, be sufficiently general. The only essential thing here is that in (20) it is the first and in (20 a) the second factor which has the subscript c . This is shown also by the symbols L (left), R (right).

Let us return to the quaternionic differential equation for the vacuum, in its first form, i. e.

$$\mathbf{D}\mathbf{F} = \mathbf{C}. \quad \text{. (VI.)}$$

$$\text{Remember that } \mathbf{D}\mathbf{D}_c = (\mathbf{T}\mathbf{D})^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} + \frac{\partial^2}{\partial l^2}$$

is the four-dimensional Laplacian, or Cauchy's $\square$,

$$\mathbf{D}\mathbf{D}_c = \square \quad \text{. (IX.)}$$

Hence, if Φ be an auxiliary quaternion and if we put $\mathbf{F} = -\mathbf{V}\mathbf{D}_c\Phi$ (since $\mathbf{F}$ is *scalarless*), or more simply if we write

$$\mathbf{F} = -\mathbf{D}_c\Phi \quad \text{. (X.)}$$

demanding at the same time that

$$\mathbf{S}\mathbf{D}_c\Phi = 0, \quad \text{. (XI.)}$$

We know already that the electromagnetic bivector $\mathbf{F}$ is a (scalarless) L -quaternion. Hence, by (IV.), if we multiply it, on the *left* side, by any physical quaternion cov. q , the resulting product will again be transformed like q . Now, the current-quaternion $\mathbf{C}$ being precisely such a quaternion, consider the product

$$\mathbf{P} = \mathbf{C}\mathbf{F}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

which, by the above, will again be transformed by $Q[\]Q$. Develop it, by (10) and (19); then

$$\mathbf{P} = \rho \left\{ \iota \mathbf{M} + \mathbf{E} + \frac{1}{c} \mathbf{pM} - \frac{\iota}{c} \mathbf{pE} \right\}$$

or, remembering that the full product $\mathbf{AB}$ is $\mathbf{VAB} - (\mathbf{AB})$,

$$\mathbf{P} = \mathbf{P}_e + \iota \mathbf{P}_m, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

where $\mathbf{P}_e$, $\mathbf{P}_m$ are the quaternions

$$\mathbf{P}_e = \rho \left\{ \frac{\iota}{c} (\mathbf{pE}) + \mathbf{E} + \frac{1}{c} \mathbf{VpM} \right\} \quad . \quad . \quad . \quad (25\ e)$$

$$\mathbf{P}_m = \rho \left\{ \frac{\iota}{c} (\mathbf{pM}) + \mathbf{M} - \frac{1}{c} \mathbf{VpE} \right\} \quad . \quad . \quad . \quad (25\ m)$$

The vector of $\mathbf{P}_e$ is the well-known *ponderomotive force*, per unit volume, and the scalar of $\mathbf{P}_e$ is ι/c times the *activity* of this force, while $\mathbf{P}_m$ is the magnetic analogue of $\mathbf{P}_e$. Notice that the whole $\mathbf{P}$, (25), though having with q the transformer $Q[\]Q$ in common, has *not* the structure of the standard q , inasmuch as it is a full *biquaternion* *. (And how each of its constituents, $\mathbf{P}_e$, $\mathbf{P}_m$, which *have* the structure of q , are transformed, we do not as yet know,—though we shall know in a moment.)

Similarly, the complementary electromagnetic bivector $\mathbf{G}$ being a (scalarless) R -quaternion, multiply it on the *right* side by $\mathbf{C}$. Then the product $\mathbf{GC}$ will, by (IV.), again be transformed by $Q[\]Q$, *i. e.* again like q . Develop it; then, by (10) and (19a),

$$\mathbf{GC} = \rho \left\{ \iota \mathbf{M} + \frac{1}{c} \mathbf{Mp} - \mathbf{E} + \frac{\iota}{c} \mathbf{Ep} \right\},$$

and this is precisely, with the same meanings of $\mathbf{P}_e$ and $\mathbf{P}_m$ as above, equal to

$$\mathbf{GC} = -\mathbf{P}_e + \iota \mathbf{P}_m. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

This again is a full biquaternion.

* In *Hamilton's*, of course, and not in *Clifford's* meaning of the word.

Now, both biquaternions, $P = CF$ and GC being transformed by the same $Q[\]Q$, this will also be the transformer of their sum, and of their difference, i. e., by (25) and (26), of P_m and of P_e .

Thus we see that not only P but also its constituents P_e and P_m , taken separately, are cov. q ; and since each of them has also the structure of q^* , both P_e and P_m are physical quaternions, cov. q .

They are given explicitly by (25e), (25m), and may, by the above, be written also

$$P_e = \frac{1}{2} \{ CF - GC \} \quad . \quad . \quad . \quad (27e)$$

$$P_m = -\frac{i}{2} \{ CF + GC \} \quad . \quad . \quad . \quad (27m)$$

It is true that (at least on the ground of the fundamental electronic equations) only P_e has an immediate physical meaning, and not P_m . But this does not seem to me a disadvantage. On the contrary; since our stock of physical quaternions, as the reader will certainly have observed, is as yet not very big, it may be better to have one more.

P_e corresponds to the "Viererkraft" † and might consequently be called here the *force-quaternion*. It has a dynamic vector and an energetic scalar, as observed above. As to P_m , it is of no importance to give it (at least for the "vacuum") any special name. On the other hand, the whole P , which may possibly turn out to be more convenient for the quaternionic treatment of Relativity, might be called the *dynamical ‡ biquaternion*, and be looked on as the standard of physical biquaternions, in the same manner as q , F have been the standards of physical quaternions and of physical bivectors, respectively §.

Now, using the quaternionic differential equation (VI.), or $C = DF$, the formula (27e) for P_e may be written

$$2P_e = DF.F - G.DF, \quad . \quad . \quad . \quad (28)$$

and similarly (27m) for P_m , the *dot* being a separator, as

* Namely an imaginary scalar and a real vector.

† See Laue, *loc. cit.*, § 15.

‡ Notwithstanding that it is partially energetic.

§ It is worth noticing again that F (plus an invariant and consequently unessential scalar) and P may be regarded as alternating products of 2 and of 3 physical quaternions, respectively. From this standpoint q , F , P and their respective companions might be considered as quaternionic entities of the 1st, 2nd, and 3rd degree, respectively.

regards the differentiating action of D . In (28) the force-quaternion P_e is immediately expressed by the electromagnetic bivector $\mathbf{F}$ and its complementary $\mathbf{G}$. Thus, the formula (28) is adapted for showing the properties of the Maxwellian stress and of the electromagnetic momentum along with the flux and the density of energy, in correspondence to the equivalent formula of Minkowski's four-dimensional system.

But, since we already know everything about the behaviour of each constituent of P , *i. e.* of P_e , P_m , we may dismiss them altogether and use more conveniently the full *dynamical biquaternion* P , as defined by (24). Thus, using again the equation (VI.), we shall have, more simply,

$$P = D[\mathbf{F} \cdot \mathbf{F}], \quad \text{ (XIV.)}$$

where the purpose of the brackets is only to emphasize the circumstance that $\mathbf{F} \cdot \mathbf{F}$ plays the part of a *dyad*. This will lead us to the quaternionic treatment of questions regarding stress, and localization and flux of energy.

But these fundamental dynamical questions will best be postponed and reserved for a future publication, in which also the quaternionic treatment of the electrodynamics of ponderable bodies and of some other relativistic subjects will be given.

November, 1911.

LXXVII. *On the Propagation of Periodic Æther Disturbance.* By ANDREW STEPHENSON*.

1. **S**INCE the Röntgen rays do not exhibit refraction, the velocity of transmission of æther disturbance through a medium depends *only* upon forced oscillations set up within the molecule, the æther being otherwise unaffected by the presence of the material particles †.

2. If the æther is treated as an elastic solid the presence of resonators in the case of periodic disturbance is equivalent to a change in the density, so that a material non-crystalline medium and the æther differ optically only in density.

* Communicated by the Author.

† As a deduction it may be noted that any deviation from the $(\mu^2 - 1)/D$ formula for the refraction of a compound or mixture, derived from the atomic refraction equivalents, is the result of deformation of the atoms, or of interatomic vibration, and cannot be subject to any general 'law.'

The observed magnitude of reflexion when the displacement is at right angles to the plane of incidence is in agreement with this fact.

When the displacement is in the plane of incidence * the agreement holds, we shall find, only *if the velocity of the irrotational wave is the same in all media*. If this velocity is relatively large the energy dissipated in irrotational motion is negligible.

The equations of motion are

$$\rho \frac{d^2 \xi}{dt^2} = \frac{d}{dx} \left(\frac{d\xi}{dx} + \frac{d\eta}{dy} \right) + n \frac{d}{dy} \left(\frac{d\xi}{dy} - \frac{d\eta}{dx} \right), \quad . \quad . \quad . \quad (i.)$$

$$\rho \frac{d^2 \eta}{dt^2} = \frac{d}{dy} \left(\frac{d\xi}{dx} + \frac{d\eta}{dy} \right) - n \frac{d}{dx} \left(\frac{d\xi}{dy} - \frac{d\eta}{dx} \right), \quad . \quad . \quad . \quad (ii.)$$

with ρ different in the two media, and at the boundary

$$\xi, \eta, \frac{d\xi}{dx} \quad \text{and} \quad \frac{d\eta}{dy} \quad \text{are continuous.}$$

The value of ρ in any material medium may depend upon the nature of the radiation, whether equivoluminal or irrotational.

From (i.) and (ii.)

$$\rho \frac{d^2}{dt^2} \left(\frac{d\xi}{dx} + \frac{d\eta}{dy} \right) = \left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} \right) \left(\frac{d\xi}{dx} + \frac{d\eta}{dy} \right), \quad . \quad . \quad . \quad (iii.)$$

$$\rho \frac{d^2}{dt^2} \left(\frac{d\xi}{dy} - \frac{d\eta}{dx} \right) = n \left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} \right) \left(\frac{d\xi}{dy} - \frac{d\eta}{dx} \right), \quad . \quad . \quad (iv.)$$

where ρ' is the effective density for the irrotational wave.

For the incident and reflected waves

$$\begin{aligned} \xi &= -\sin \theta \cos \kappa (x \cos \theta + y \sin \theta - ct) \\ &\quad + r \sin \theta \cos \{ \kappa (-x \cos \theta + y \sin \theta - ct) - a \}, \\ \eta &= \cos \theta \cos \kappa (x \cos \theta + y \sin \theta - ct) \\ &\quad + r \cos \theta \cos \{ \kappa (-x \cos \theta + y \sin \theta - ct) - a \}; \end{aligned}$$

in the transmitted wave

$$\begin{aligned} \xi_1 &= -s \sin \theta_1 \cos \{ \kappa_1 (x \cos \theta_1 + y \sin \theta_1 - c_1 t) - \beta \}, \\ \eta_1 &= s \cos \theta_1 \cos \{ \kappa_1 (x \cos \theta_1 + y \sin \theta_1 - c_1 t) - \beta \}; \end{aligned}$$

* The discussion due to Green (1840) is still accepted: his conclusions are erroneous.

and in the irrotational boundary disturbances

$$\xi = -pe^{\kappa \sin \theta \sqrt{1 - \frac{c^2}{V^2} \operatorname{cosec}^2 \theta}} \cos \{ \kappa (y \sin \theta - ct) - \epsilon \},$$

$$\eta = \frac{p}{\sqrt{1 - \frac{c^2}{V^2} \operatorname{cosec}^2 \theta}} e^{\kappa \sin \theta \sqrt{1 - \frac{c^2}{V^2} \operatorname{cosec}^2 \theta}} \sin \{ \kappa (y \sin \theta - ct) - \epsilon \},$$

and

$$\xi_1 = p_1 e^{-\kappa_1 \sin \theta_1 \sqrt{1 - \frac{c_1^2}{V_1^2} \operatorname{cosec}^2 \theta_1}} \cos \{ \kappa_1 (y \sin \theta_1 - c_1 t) - \epsilon_1 \},$$

$$\eta_1 = \frac{p_1}{\sqrt{1 - \frac{c_1^2}{V_1^2} \operatorname{cosec}^2 \theta_1}} e^{-\kappa_1 \sin \theta_1 \sqrt{1 - \frac{c_1^2}{V_1^2} \operatorname{cosec}^2 \theta_1}} \sin \{ \kappa_1 (y \sin \theta_1 - c_1 t) - \epsilon_1 \},$$

where V and V_1 are the velocities of the irrotational waves.

From the boundary conditions, *if, and only if*, $V = V_1$,

$$\alpha = \beta = \epsilon = \epsilon_1 = 0,$$

$$r = \frac{\tan (\theta_1 - \theta)}{\tan (\theta_1 + \theta)},$$

$$s = \frac{\cos \theta}{\cos \theta_1} (1 + r),$$

$$p = p_1 = \cos \theta \tan (\theta_1 - \theta).$$

No restriction is placed upon the magnitude of V , but the solution fails when θ is in the neighbourhood of $\sin^{-1} c/V$, and for values less than $\sin^{-1} c/V$ the boundary disturbances become simple periodic functions of x : in both cases, therefore, no steady state is reached and energy is dissipated in irrotational motion.

The solution in the case of total internal reflexion may be obtained on replacing the transmitted train by the corresponding equivoluminal motion parallel to the boundary.

3. In a medium in which the molecules are similarly oriented the velocity depends on the direction of transmission. Let the direction of a resonator be (l', m', n') and its relative intensity a . Then for a periodic disturbance with the displacement in the direction (l, m, n) the forced oscillation is of intensity

$$a(l'l + mm' + nn'),$$

so that the whole system is equivalent to the three forced oscillations

$$l\Sigma al'^2 + m\Sigma al'm' + n\Sigma an'l', \quad l\Sigma al'm' + m\Sigma am'^2 + n\Sigma am'n', \\ l\Sigma an'l' + m\Sigma am'n' + n\Sigma an'^2.$$

The effect of the resonators is therefore equivalent to changes in the density of the æther along the axes for which

$$\Sigma al'm', \quad \Sigma am'n', \quad \text{and} \quad \Sigma an'l'$$

are zero.

The irrotational wave has the same velocity along the three axes. The equations of motion are therefore

$$\ddot{\xi} = v_x^2 \nabla^2 \xi + (V^2 - v_x^2) \frac{d}{dx} \left(\frac{d\xi}{dx} + \frac{d\eta}{dy} + \frac{d\zeta}{dz} \right), \quad \dots \quad (\text{v.})$$

$$\ddot{\eta} = v_y^2 \nabla^2 \eta + (V^2 - v_y^2) \frac{d}{dy} \left(\frac{d\xi}{dx} + \frac{d\eta}{dy} + \frac{d\zeta}{dz} \right), \quad \dots \quad (\text{vi.})$$

$$\ddot{\zeta} = v_z^2 \nabla^2 \zeta + (V^2 - v_z^2) \frac{d}{dz} \left(\frac{d\xi}{dx} + \frac{d\eta}{dy} + \frac{d\zeta}{dz} \right). \quad \dots \quad (\text{vii.})$$

Hence for the train

$$\xi, \eta, \zeta = p, q, r \cos \kappa (lx + my + nz - ct),$$

$$\frac{l^2}{c^2 - v_x^2} + \frac{m^2}{c^2 - v_y^2} + \frac{n^2}{c^2 - v_z^2} = 0, \quad \dots \quad (\text{viii.})$$

and the displacement is in the direction

$$\left(\frac{V^2 - v_x^2}{c^2 - v_x^2} l, \quad \frac{V^2 - v_y^2}{c^2 - v_y^2} m, \quad \frac{V^2 - v_z^2}{c^2 - v_z^2} n \right),$$

and therefore lies in the plane

$$\begin{vmatrix} x & y & z \\ l & m & n \\ \frac{l}{c^2 - v_x^2} & \frac{m}{c^2 - v_y^2} & \frac{n}{c^2 - v_z^2} \end{vmatrix} = 0.$$

It is noteworthy that the plane of polarization and the velocity are independent of the velocity of the irrotational wave, although the motion involves change of volume.

4. It is now possible to determine the circumstances of

the reflexion and refraction when radiation is incident on a crystal at a surface which is normal to a principal axis, the planes of incidence and polarization containing the other axes.

With the same notation as before, in the transmitted wave

$$\xi_1 = -\frac{V^2 - v_x^2}{V^2 - v_y^2} \cdot s \sin \theta_1 \cos \{ \kappa (x \cos \theta + y \sin \theta - ct) - \beta \},$$

$$\eta_1 = s \cos \theta_1 \cos \{ \kappa (x \cos \theta + y \sin \theta - ct) - \beta \}.$$

The boundary disturbance in the crystal is found to be the same as in an isotropic medium. The equations expressing the boundary conditions are at once obtainable, and the solution follows.

There is in general a change of phase at reflexion, but it vanishes if V is very large, the solution then being identical with that for an isotropic medium.

From the phenomena of the reflexion *the velocity of the irrotational wave can be determined, or its relative largeness established* *.

January, 1912.

LXXVIII. On the Secondary Rays excited by the Alpha Rays from Polonium.—I. By V. E. POUND, M.A.†

1. Introduction.

RECENT researches have shown that radioactive materials from which α rays are sent off also emit a radiation of negatively charged particles, which will not ionize a gas, and which has been called δ rays. The other characteristics of this radiation are that it is easily absorbed, it is easily deflected by a magnetic field, and it is stopped by a small positive charge placed upon the radioactive substance emitting it. Still later researches by Logeman ‡ and Aschkinass § have shown that when α rays fall on a polished piece of metal such as copper, this metal emits a secondary radiation with characteristics similar to those of the δ rays. Further,

* It is hardly necessary to note that it is zero according to the electromagnetic theory.

† Communicated by Professor J. C. McLennan: read before the Canadian Institute, Toronto, January 13, 1912.

‡ Logeman, Proc. Roy. Soc. Series A, vol. lxxviii. Sept. 6, 1907.

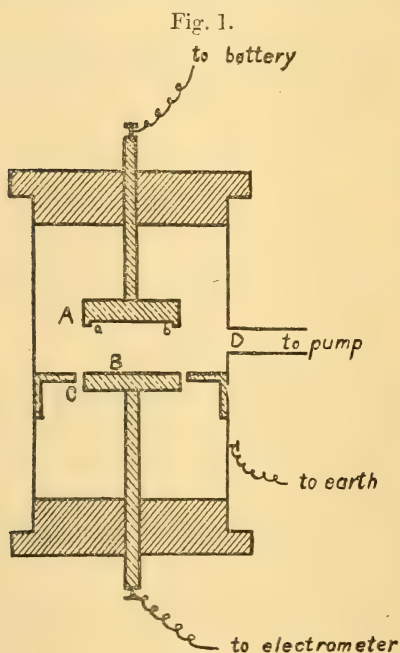
§ E. Aschkinass, *Ann. der Phys.* no. 12 (1908).

it has been found by Duane * that the α rays lose their power to produce secondary rays at the same time that they lose their charge and their power to ionize a gas.

The present paper describes some experiments on these secondary rays produced by the α rays of polonium. The apparatus employed at first was somewhat similar to that used by Logeman when he established the existence of this secondary radiation from metals bombarded by α rays. In the experiments to be described exhaustions were made with a Gaede pump, and the pressures were measured with a McLeod gauge.

2. Description of Apparatus.

The apparatus used in the initial experiments is shown in fig. 1. It consisted of a brass cylinder about 4 cm. in



diameter and 9 cm. in length, which had an ebonite plug fitting into each end. Through one of these plugs was led a brass rod which carried a round brass electrode B, about 15 mm. in diameter. The electrode B was surrounded by a circular guard-ring C.

Through the other plug was led another brass rod, and it

* Duane, *Comptes Rendus*, May 25, 1908.

carried the second electrode, A. A circular surface, *ab*, of this electrode A, about 15 mm. in diameter, was coated with a deposit of polonium. The distance between the polonium deposit and the surface of the electrode B was 6 mm. The polonium and the surface of the electrode B were coaxial. The brass cylinder, which was made air-tight with wax, was connected to the McLeod gauge and the Gaede air-pump by a tube D. The polonium-coated electrode, A, was connected to a battery, and the brass electrode, B, to a sensitive quadrant electrometer. The brass cylinder surrounding the two electrodes was connected to earth.

3. Repetition of Logeman's Experiment.

The experiment which Logeman* made was first repeated, and the results obtained were similar to those obtained by him with identical electrical fields. The experiment was conducted in the following manner. By means of the Gaede pump the air was pumped out from the apparatus to as low a vacuum as possible. The pressure of the air was measured by means of the McLeod gauge, and when the pressure became so low that the McLeod gauge could not measure it, which was less than 1/1000 of a millimetre of mercury, the polonium was connected to earth, and the rate of charging of the brass electrode opposite was measured by means of the electrometer. Then the polonium was charged to a series of different potentials by means of a storage-battery, and the corresponding rates of charging of the brass electrode were ascertained. Throughout the experiment the Gaede pump was kept going continuously in order to withdraw any gas which might come from the walls of the apparatus.

The results which were obtained are given in Table I.

TABLE I.

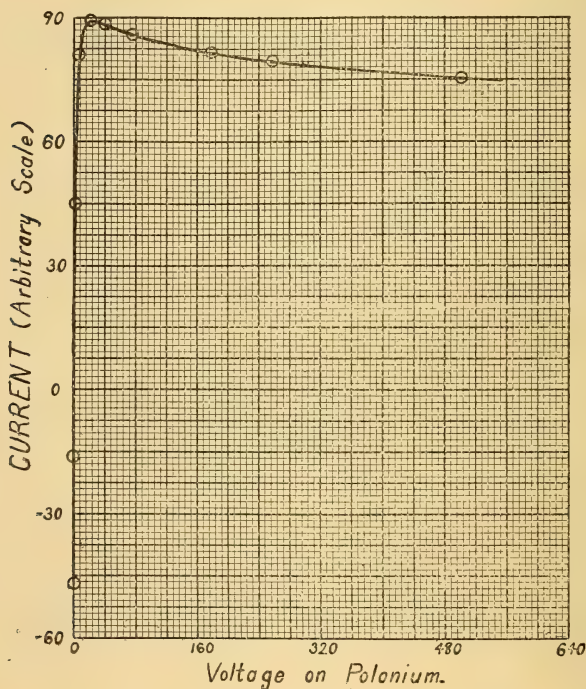
Pressure less than .001 mm. Distance between electrodes 6 mm.

Voltage on polonium.	Rate of charging.
0 volts	-49
.44 "	-16
2.1 "	45.1
7	81
19	89.5
40	88.5
76	86
179	82
258	80
502	75.5

* Logeman, Proc. Roy. Soc. vol. lxxviii. Sept. 6, 1907.

In column 1 is given the voltage applied to the polonium, and in column 2 the charge gained per minute by the brass electrode opposite the polonium, as measured by the quadrant electrometer. A curve representing these results is shown in fig. 2.

Fig. 2.



It is evident from the results given in the Table, and from the curve, that when the polonium was at zero voltage the charge gained by the brass electrode was negative. It is also evident that as the voltage on the polonium was increased positively the charge gained by the electrode increased from a negative charge to a positive one, and that at a potential of about 20 volts the rate of charging became a maximum. This result agrees with the numbers recorded in his paper, a few of which are given in the following table. The results can be readily compared, because the distance between the polonium and the opposite electrode was about the same as that in Logeman's apparatus.

Logeman's Results.

Distance between electrodes 5 mm.

Potential on polonium.	Reading of current to electrode.
0 volts	-58.0
2 „	86
12 „	182
14 „	185

It will be seen, however, from the curve, that as the potential on the polonium was increased beyond 20 volts, the rate of charging of the electrode gradually decreased. This effect does not appear to have been observed by Logeman. In searching for the explanation of it, further interesting properties of the secondary rays were found by the writer which have not as yet been noted by other experimenters.

Before seeking for an explanation of the results given in Table I. and shown graphically in fig. 2, it is necessary to enumerate the different currents which would give a charge to the brass electrode B. In the first place there would be a current due to the passage of the α rays from the polonium across the space separating the polonium from the electrode. Since the α rays are positively charged particles this current would charge the electrode positively. Then there would be a current of negatively charged particles from the polonium which would reach the electrode. This current is known as the δ radiation, and always accompanies a discharge of α particles. The passage of this current would give a negative charge to the electrode. Again, there would be a stream of negatively charged particles emitted by the electrode. The researches of Aschkinass and Logeman have proven this stream to exist whenever a substance is bombarded by α rays, and it has been called the secondary radiation. The emission of this stream of negatively charged particles would have the effect of charging the electrode positively. Finally, there would be a current through the air in the chamber, due to the ionization of the air by the α rays. The last current would charge the electrode positively, since the polonium was positively charged. This current, which we will call the ionization current, would be, in all probability, very small on account of the small quantity of gas in the chamber.

Let us now consider what would be the effect on these different currents of increasing the positive potential on the

polonium from zero upwards. The number of α particles emitted per second by the polonium could not be changed by increasing the potential, for it is found impossible to change the rate of emission of the α , β , and γ rays from the radioactive substances by any known agency. The increase of the potential on the polonium might, however, increase the speed with which the α particles passed from the polonium to the electrode. If this were the case, since it has been shown by different experimenters, including Geiger and Marsden*, that α rays are reflected to some extent from the substances they strike, this increase in velocity might cause a more profuse reflexion of the α rays from the electrode. Hence, as the potential was increased there would be fewer and fewer α particles which would remain attached to the electrode, and this would cause the positive rate of charging of the electrode to decrease.

The effect of increasing the positive potential on the polonium could only tend to retard more and more of the δ rays which are negatively charged and of slow velocity. Hence, on account of the stopping of these rays, the rate of charging of the electrode positively must have increased. In fact the sharp rise in the first part of the curve shown in fig. 2 has been attributed by Logeman and others, and very probably correctly so, to the stoppage of the δ rays by the positive charge on the polonium.

Again, the increase of the positive charge on the polonium must tend to produce a freer discharge of negative electricity from the electrode, since a positive charge on the polonium attracts negative from the electrode. The primary cause of this discharge would be, of course, the bombardment of the electrode by the α rays, and this is what we have called the secondary radiation. An increase in the amount of secondary radiation discharged from the electrode would increase the rate at which the electrode charged positively.

Finally, the increase of potential on the polonium would have the effect of increasing the ionization current from the polonium to the electrode through the gas, and this would cause the positive rate of charging of the electrode to increase, since the charges on the polonium were positive. There is, however, one factor which may have influenced the experiment, and which must be considered here, and that is that the Gaede pump was kept going continuously in order to

* Geiger and Marsden, Proc Roy. Soc. Series A, vol. lxxxii. July 31, 1909.

keep the pressure low. The readings were not taken until the pressure was less than $1/1000$ of a mm. of mercury, but yet, the pressure may have decreased still further while the readings were being taken, and on account of the decrease in the pressure the ionization current may have also decreased. It is evident that this would cause a decrease in the positive rate of charging of the electrode.

It is seen, therefore, that, according to the above explanations of the charging of the electrode by the different currents, there are only two things which might cause a decrease in the rate of charging of the electrode positively, as the potential on the polonium was raised positively. Either there might be a more profuse reflexion of α rays from the electrode, and so a reduction in its rate of charging, or there might be a gradual decrease in the ionization current due to the lowering of the pressure of the air in the apparatus.

Now it is evident from the curve given in fig. 2 that there was a gradual decrease in the rate of charging of the electrode after the potential of the polonium was increased beyond 20 volts. In order to find out how much of this decrease or whether any at all was due to the withdrawal of more air from the apparatus after it was exhausted to a very low pressure, the experiments described in the following section were performed.

4. Ionization Experiments.

In the first experiment the polonium was charged to a positive potential of 77 volts. It was found, § 3, that with the polonium at this potential the δ radiation from A was practically all stopped. The Gaede pump was started and the air which had stood in the apparatus for a week, at atmospheric pressure, was pumped out until the pressure as measured by the McLeod gauge was less than $1/1000$ of a mm. of mercury. The time taken by the pump to do this was about 15 minutes. Then, while the pump was kept continuously going, readings were taken of the rate of charging of the electrode at different intervals of time. It was hoped in this way to get some idea of the effect of the withdrawal of the air on the ionization current between the polonium and the electrode. In Table II. the results obtained are given.

TABLE II.

Air in Apparatus.

Brass electrode B. Voltage on polonium = 77 volts.

Time.	Current to electrode.
0 minutes	97
5 "	81
10 "	76
15 "	67.5
25 "	64
120 "	59
130 "	59

The first column states the time between any reading and the initial reading, while the second column gives the rate at which the electrode charged up.

As shown by the Table, the rate at which the electrode gained a charge decreased with the time, and finally came to a constant value.

In this experiment the polonium was at the same voltage all the time, hence there could be no change in the rate of charging of the electrode, due to a change in voltage. Therefore, according to the theory of the charging of the electrode as outlined in the previous section, the gradual drop in the rate of charging of the electrode as the time passed could only be due to a decrease in the ionization current through the gas. This decrease could be attributed to a further withdrawal of air from the apparatus by the pump after the pressure had been reduced to less than $1/1000$ of a mm. of mercury. If this were the case this decrease in ionization would continue until the pressure of the air in the vessel reached a constant value. Then the air withdrawn by the pump would be equal to the air which oozed out from the sides of the vessel. The final constant value for the rate of charging of the electrode would denote this equilibrium condition between the air taken away by the pump and the air which oozed out from the walls of the chamber.

If the above explanation is correct, then, if the apparatus were filled with another gas than air such as hydrogen, and the experiment were repeated as with the air, there would again be a final pressure, and also a final ionization current through the hydrogen. But on account of the different nature of the two gases this final ionization current would be different in the two cases, and hence the final rate of charging of the electrode would also be different in the two cases.

In order to find out whether this was true the apparatus was filled with pure and dry hydrogen and left standing over night at atmospheric pressure. Previously, the apparatus had been depleted as much as possible of air by keeping it at low pressure and pumping out the air which came from the walls. The polonium was charged to a positive potential of 77 volts, the hydrogen was pumped out to less than 1/1000 of mm. of mercury, and then readings were taken as with the air of the rate of charging of the brass electrode, and are given in the following Table :—

TABLE III.

Hydrogen in Apparatus.

Brass electrode B. Voltage on polonium = 77 volts.

Time.	Current to electrode.
0 minutes	86.6
6 "	73.1
16 "	65.1
31 "	62.6
91 "	59.5
95 "	59.5
121 "	59.0

It will be seen on looking at the Table that there was a decrease in the rate of charging of the electrode with the time, as with the air. On comparing Table II. and Table III. it will also be seen that the initial rates of charging of the electrode were different with the two gases, but the final rates were the same. The experimental results, therefore, did not agree with the predicted results, for it was predicted that the final rates of charging of the electrode would be different using two different gases on account of the difference in the final ionization currents through air and through hydrogen. The experimental results go to show that the final ionization currents were the same. This seemed hardly possible on account of the difference in density of the two gases. Another explanation of the reason why these two final rates of charging were the same was therefore looked for. The simplest one that suggested itself was that when the final rates of charging were the same there was such a small quantity of either air or hydrogen in the apparatus that practically no ionization current existed.

The next question that naturally arose was whether all of the drop in the rate of charging of the electrode was due to a drop in the ionization current through the air and through the hydrogen. In order to answer this question the following

experiment was performed. It was found that if arc-light carbon was used as the electrode instead of brass, there was a greater drop in its rate of charging than when brass was used under the same conditions. Accordingly, the brass electrode was removed from the apparatus and a similarly shaped piece of carbon was put in. The polonium was charged to a positive potential of 78 volts, and the pump was started exhausting the air, which was initially at atmospheric pressure. Seven minutes after the pump was started readings were taken of the pressure of air in the vessel as measured by the McLeod gauge, and the rate of charging of the carbon electrode. Similar readings were made at different intervals of time after the initial readings. The pump was kept going continuously throughout all the readings. The results are given in the following Table:—

TABLE IV. *a.*

Air in Apparatus.

Carbon electrode. Charge on polonium = 78 volts.

Pressure of air in vessel.	Time from initial reading.	Current to electrode.
·008 mm.	0 minntes	46
·004 "	1 "	42
·002 "	5 "	38
<·001 "	15 "	34·5
<·001 "	30 "	31·5
<·001 "	60 "	29·0
<·001 "	120 "	29

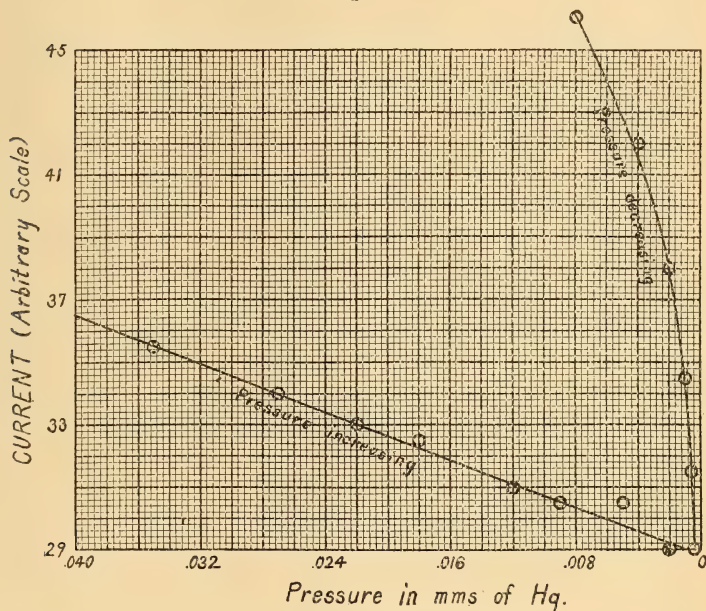
The pump was then stopped, and while the pressure gradually increased as the air flowed out from the walls of the apparatus, the series of readings were continued and are given below.

TABLE IV. *b (continued).*

Pressure of air in vessel.	Time from initial reading.	Current to electrode.
·001 mm.	123 minutes	29
·002 "	126 "	29
·005 "	129 "	30·5
·009 "	134 "	30·5
·012 "	139 "	31
·018 "	146 "	32·5
·022 "	153 "	33
·027 "	161 "	34
·035 "	171 "	35·5

If the results that were obtained while the pressure of the air was decreasing are compared with the results obtained while the pressure was increasing, as given in Table IV., and shown graphically in fig. 3, it will be seen that at any given

Fig. 3.



pressure the rate of charging of the electrode was greater as the pressure was decreasing than as it was increasing. It will also be seen that the rate of charging at a pressure of .035 mm. of mercury as the pressure was increasing was very much less than the rate of charging at much smaller pressures as the pressure was decreasing. These results show clearly then, that the decrease in the rate of charging of the electrode as the air was pumped out of the apparatus was not all due to a decrease in the ionization current through the gas. For since the ionization current is only dependent on the pressure of the air in the chamber, it should have the same value at like pressures, whether the pressure was decreasing or increasing.

If the decrease in the rate of charging of the electrode with the time was not all due to a decrease in the ionization current through the gas there must be some other reason for this decrease. As shown in § 3, there are three other currents which cause the electrode to charge up besides the

ionization current. These are the α ray current from the polonium, the δ ray current from the polonium, and the secondary ray current from the electrode. It has been shown by an experiment in § 3 that a positive potential of 20 volts is sufficient to stop practically all the δ ray current. Therefore, in this experiment, the only currents which charged up the electrode besides the ionization current were the α ray current and the secondary radiation current. Either both or one of these currents, then, must have had a decrease in intensity as well as the ionization current in order to produce the total decrease in the rate of charging of the electrode as found by experiment. The decrease in intensity of the α rays from polonium with the time has been studied by various experimenters, and they have found the intensity falls to half value in 140 days. The time taken by the experiment was about three hours, so that in this short interval of time the decrease in intensity of the α rays was practically nothing. Hence there must have been a considerable decrease in the intensity of the secondary radiation emitted by the carbon from the time when the first reading of the rate of charging of the electrode was taken.

The causes, then, of the decrease in the rate of charging of the electrode with the time as found in the above experiment was a small decrease in the ionization current through the air as the pressure was reduced, and a large decrease in the secondary rays sent off by the carbon. The same causes will account for the decrease in the rate of charging of the brass electrode used in the first two experiments of this section, and must also be considered when the results of the experiment described in § 3 are explained. Before continuing experiments with the object of a further elucidation of the results described in § 3, it was thought well first to make an extended study of the phenomenon of the decrease in the intensity of the secondary radiation as made evident by the foregoing experiments.

5. Experiments on the "Fatigue" of Secondary Rays.

The experiments described in § 4 show that there was a decrease in the secondary radiation sent off by carbon bombarded by α rays as the air was pumped out of the apparatus in which the carbon was placed. This decrease may be called a fatigue of the secondary rays, for the effect is similar to that observed in the case of the photoelectric fatigue. The phenomenon of the photoelectric fatigue has

been studied extensively, and various reasons have been suggested for it. One of the reasons which have been advanced is that the substance which emits the photoelectric radiation becomes impoverished of available negative corpuscles. If the fatigue in the present experiments were due to a decrease in the number of available negative corpuscles, this decrease must have been all at the surface, since the exciting α rays have only a small penetrability. If the decrease were due to this cause, it is probable that if air were admitted into the apparatus again, the electrode would regain its normal condition. To test this the following set of experiments was performed.

A fresh piece of carbon was placed in the apparatus, a positive charge of 80 volts was put on the polonium, the Gaede pump was started, and at a definite interval of time after the starting of the pump readings were taken of the rates of charging the carbon electrode, and of the corresponding pressures of air in the apparatus. These readings were continued until there was practically no further decrease in the rate of charging of the electrode.

The readings are given in the following Table :—

TABLE V.

Air in Apparatus.

Fresh carbon electrode. Charge on polonium = 80 volts.

Pressure of air in vessel.	Time from initial reading taken 7 minutes after starting pump.	Current to electrode.
·007 mm.	0 minutes	124·7
·002 "	5 "	78·2
·001 "	15 "	50·7
∧ ·001 "	25 "	41·2
∧ ·001 "	41 "	35·2
∧ ·001 "	65 "	31·2
∧ ·001 "	87 "	28·2
∧ ·001 "	123 "	26·2

The carbon was left in the evacuated apparatus, bombarded by α rays from the polonium, for one week in order that it should get thoroughly fatigued in the production of secondary rays. Then the apparatus was filled with air at atmospheric pressure and again left standing for one week. At the end of this time the experiment described above was repeated, and the readings are given below.

TABLE VI.

Air in Apparatus.

Fatigued carbon electrode. Charge on polonium = 80 volts.

Pressure of air in vessel.	Time from initial reading taken 7 minutes after starting pump.	Current to electrode.
·008 mm.	0 minutes	32·7
·003 "	5 "	30·2
·002 "	15 "	29·2
·001 "	36 "	24·7
<·001 "	60 "	22·3

After this experiment was completed the apparatus was immediately filled with air at atmospheric pressure and left standing for 22 hours. Then the above experiment was again repeated with the following results.

TABLE VII.

Air in Apparatus.

Fatigued carbon electrode. Charge on polonium = 80 volts.

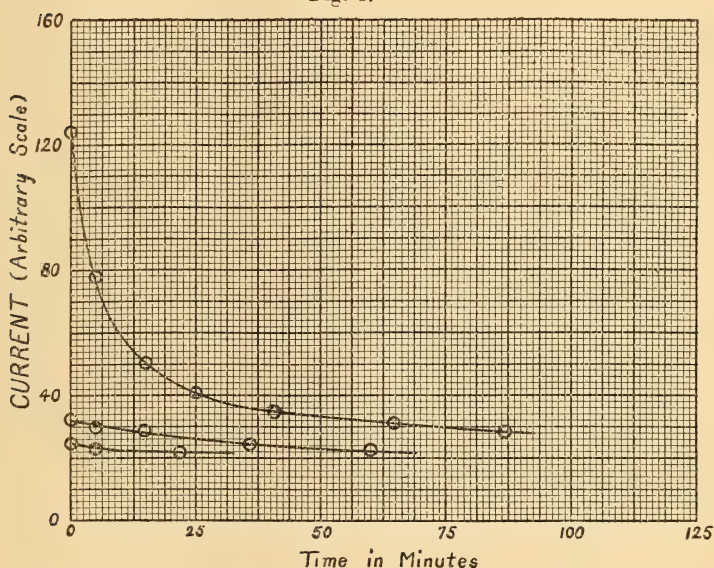
Pressure of air in vessel.	Time from initial reading taken 7 minutes after starting pump.	Current to electrode.
·004 mm.	0 minutes	25·3
·001 "	5 "	22·8
<·001 "	22 "	21·8

The results given in the last two columns of Tables V.-VII. are represented by curves shown in fig. 4. The upper curve is plotted from the results given in Table V., the middle curve from Table VI., and the lower curve from Table VII.

It will be seen on looking at the curves that each has a gradual drop. This drop represents both the decrease as time went on in the rate at which the carbon electrode sent out secondary rays, and the decrease in the ionization current across the air-gap between the polonium and the electrode, beginning at a certain definite interval of time after the first air was taken from the apparatus. It will be seen also on comparing the curves that the initial point of the upper curve is much higher than the initial points of the lower curves. Also the upper curve decreases much more quickly than the lower curves, until, finally, the three curves all come

together. Now the decrease in the ionization current through the air space with the time would be the same in all three experiments, because this decrease is dependent on the air pressure and, as the pump was kept going regularly, the air pressure, in all three cases, would be the same at equal intervals of time after the pump was started. Hence, since the upper curve shows a much greater drop than the two

Fig. 4.



lower curves, there must have been a much greater decrease in the secondary radiation in the first experiment than in the two later experiments. Therefore there must have been a much more copious emission of secondary rays at the beginning of the first experiment than at the beginning of the other two experiments. This is indicated by the height of the initial point of the upper curve above the initial points of the other two curves.

The above experiments, therefore, show that when fresh carbon is used as an electrode and subjected to bombardment by α rays and the air withdrawn from around the carbon, there is a great decrease in the secondary rays as time goes on, until finally the secondary rays emitted reach a constant value. Then, if the carbon is kept *in vacuo* for some time (one week) it will not regain its primary power of emitting secondary rays by being surrounded again by air while still under bombardment by α rays even for periods of time extending up to 22 hours.

The next experiments that were performed were for the purpose of finding out whether this same carbon would send out secondary rays with its initial intensity if it were placed in an atmosphere of hydrogen instead of air. The apparatus was first filled with dry hydrogen, produced from zinc and acidulated water, and left at atmospheric pressure for four hours. Then, as before, a positive charge of 80 volts was put on the polonium, the pump was started, and at a definite interval of time after starting the pump, a series of readings were taken on the rates at which the carbon electrode charged up, and on the corresponding pressures of the hydrogen in the apparatus. The readings are given in the following Table.

TABLE VIII.
Hydrogen in Apparatus.

Fatigued carbon electrode. Charge on polonium=80 volts.

Pressure of hydrogen in vessel.	Time from initial reading taken 4 minutes after starting pump.	Current to electrode.
·006 mm.	0 minutes	24·5
·003 "	6 "	23·0
<·001 "	15 "	22
<·001 "	31 "	22
<·001 "	56 "	22

Next the apparatus was filled with hydrogen at atmospheric pressure and left standing for eighteen hours. A series of readings was taken as before, and these are given below.

TABLE IX.
Hydrogen in Apparatus.

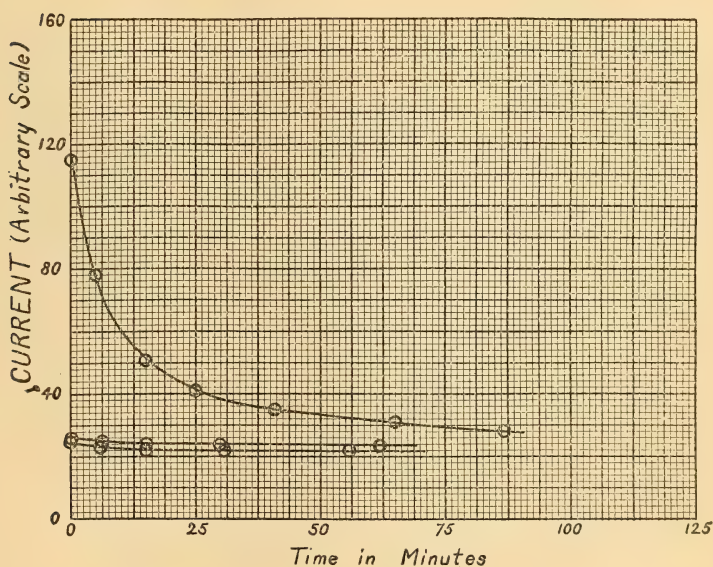
Fatigued carbon electrode. Charge on polonium=80 volts.

Pressure of hydrogen in vessel.	Time from initial reading taken 4 minutes after starting pump.	Current to electrode.
·005 mm.	0 minutes	25·7
·002 "	5 "	24·7
<·001 "	15 "	24
<·001 "	30 "	23·5
<·001 "	62 "	23·5

It will be noticed that in these two last experiments with the hydrogen the first reading was taken four minutes after the pump was started, while in the three experiments with the air the first reading was taken seven minutes after the pump was started. The reason for this was that the pump reduced the pressure of the hydrogen much more quickly than the air, and it was desired to take the first readings for both hydrogen and air at approximately the same pressure.

From the results given in the last two columns of Tables VIII. and IX. the two lower curves of fig. 5 are

Fig. 5.



plotted, while the upper curve of fig. 5 is plotted from the results given in the last two columns of Table V. The latter curve pictures the way in which the rate of charging of the fresh carbon electrode decreased with the time, while the former curves show how the rate of charging of the fatigued carbon electrode, which had been left in hydrogen at atmospheric pressure, decreased with the time.

It will be noticed that there is hardly any drop in the lower curves, while the drop in the upper curve is considerable. It will be seen also that the rate of charging of the fatigued electrode, as indicated by the lower curves, is nearly the same as the final value of the rate of charging of the fresh

electrode as indicated by the upper curve. Hence the above experiments indicate that the carbon electrode did not regain any of its primary power of producing secondary rays by being surrounded by hydrogen at atmospheric pressure.

The above experiments, therefore, show that a carbon electrode which has been fatigued in the production of secondary rays, and left *in vacuo* for a long time, will not regain its primary power of producing secondary rays by simply being placed in an atmosphere of either air or hydrogen. Hence the fatigue of the carbon was not due to a temporary loss of available negative corpuscles, which might possibly be regained in some way from air or hydrogen when these gases are allowed to surround the carbon.

The next experiments that were tried were to find out whether a piece of carbon would regain its power of producing secondary rays if it were fatigued for a very short time only. A fresh piece of carbon was placed in the apparatus and a set of experiments similar to the ones described above was performed, except that, instead of leaving the carbon in the evacuated chamber after the current to the carbon had gained a steady value, it was left for a week with the air at atmospheric pressure. The readings taken with the fresh carbon are given in Table X., and the readings taken after the fatigued carbon had been left for a week surrounded by air at atmospheric pressure are given in Table XI.

The results given in these two Tables are graphically illustrated by the curves shown in fig. 6. The upper curve refers

TABLE X.

Fresh carbon electrode.

Air in apparatus. Charge on polonium = 82 volts.

Pressure of air in vessel.	Time from initial reading taken 7 minutes after starting pump.	Current to electrode.
·008 mm.	0 minutes	123·5
·003 "	5 "	82·5
·001 "	15 "	44·5
·001 "	30 "	29
<·001 "	60 "	22
<·001 "	90 "	19·5
<·001 "	120 "	18
<·001 "	142 "	17·5

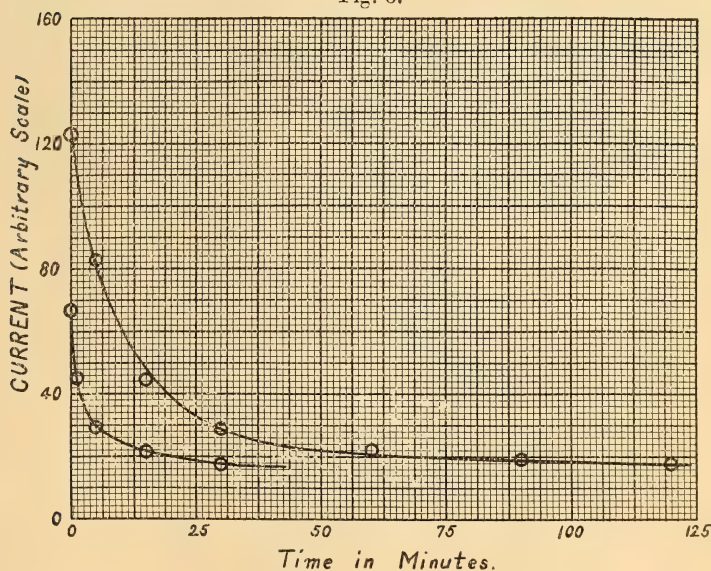
TABLE XI.

Air in Apparatus.

Fatigued carbon electrode. Charge on polonium = 84 volts.

Pressure of air in vessel.	Time from initial reading taken 7 minutes after starting pump.	Current to electrode.
·006 mm.	0 minutes	66·3 mm.
·004 "	1 "	45·3 "
·002 "	5 "	29·3 "
·002 "	15 "	21·3 "
·001 "	30 "	17·3 "

Fig. 6.



to the results in Table X., while the lower curve refers to Table XI. A comparison of these curves with the curves shown in fig. 4 makes it plain that there was a much greater recovery of the carbon fatigue when it was left *in vacuo* a very short time and then surrounded by air, than when it was left for a long time before being surrounded with air.

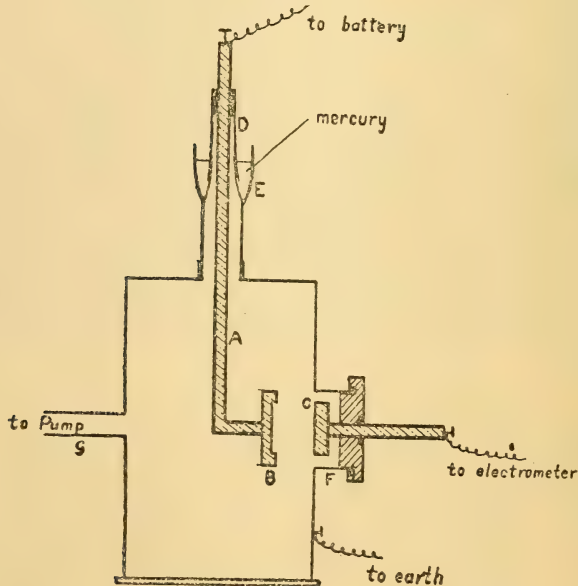
This pointed to the probability that the gas occluded in the carbon was the cause of the large decrease with the time

in the secondary radiation. For if the gas occluded in the carbon, as well as the carbon itself, produced secondary radiation, then as the exhaustion proceeded gas would ooze out of the carbon, and the secondary radiation would decrease, until all the gas which could leave had disappeared entirely from the surface of the carbon. Also, the longer the carbon was left *in vacuo* the more occluded gas would come out and the more difficult it would be for the same amount of gas to enter the carbon again. Hence this would cause the fatigue to be more permanent when the carbon was left in a vacuum a long time than when left a short time. This conclusion, it will be seen, has been amply confirmed by the experiment described above.

In order to decide definitely whether the release of the gas occluded in the carbon had to do with the decrease in the secondary rays which has been called a fatigue, a special piece of apparatus was designed and experiments were performed which will be described in the following section.

6. *Experiments showing the influence of occluded gas on the Secondary Radiation.*

Fig. 7.



The essential parts of the apparatus (fig. 7) were two parallel electrodes, B and C, in an air-tight vessel, separated

a distance of about 6 mm. The polonium, which was carried by the electrode B, could be made to face in any direction by turning the axial rod A. This rod passed through, and was sealed to, a glass tube D, which fitted over another glass tube E, so arranged that the joint could be covered with mercury and so made air-tight. The electrode C, which was made of carbon, was connected with the quadrant of an electrometer, the connecting rod passing through an ebonite plug fitted into the side of a vessel by a side tube F. Another side tube G connected the vessel to the McLeod gauge and the Gaede pump. The vessel itself, which was a cylindrical brass tube about 5 cm. in diameter and 8 cm. in length, was connected to earth. All joints were made air-tight by means of wax and solder.

The first experiment was conducted as follows. A fresh carbon electrode was placed in the apparatus, the polonium was turned away from the electrode, and the air was pumped from the vessel for over an hour with the pump going continuously. Then the polonium was charged to a positive potential of 80 volts, and turned so that it faced the carbon electrode. A reading was at once taken of the rate at which the carbon electrode charged up, and similar readings were made at suitable intervals of time afterwards. The results obtained are given in Table XII.

TABLE XII.

Fresh carbon in apparatus.

Turned polonium to face carbon 1 hour 20 minutes after pump was started. Voltage on polonium=80 volts.

Pressure of air in vessel.	Time from initial reading taken 1 h. 20 m. after starting pump.	Current to electrode.
< .001 mm.	0 minutes	122
< .001 "	5 "	123
< .001 "	15 "	124
< .001 "	30 "	122
< .001 "	60 "	123

These results show that there was no sign of a "fatigue" in the rate at which the carbon electrode charged up with the time, for the rate was practically constant throughout all the readings.

We have seen, therefore, that it is possible to get rid of the fatigue effect altogether by withdrawing the gas from the surface of the carbon before beginning the bombardment by α rays. The "fatigue," then, which has been described in the previous sections must be due to a decrease in the secondary radiation from the gas occluded at the surface of the brass or carbon electrode used.

In view of the effect which the presence of gas has on the secondary radiation it was thought well to repeat the experiment described in § 3, and first performed by Logeman. Instead of using a brass electrode a carbon electrode was used. Also the carbon was left in the vessel at low pressure for two days in order that the gas occluded in the carbon should disappear or reach a value which would be constant for the low pressure used. Then readings were taken of the rate at which the carbon electrode charged up as the positive potential on the polonium was varied from 0 volts to about 1700. The results are given in Table XIII. below, and a curve drawn from these results is shown in fig. 8.

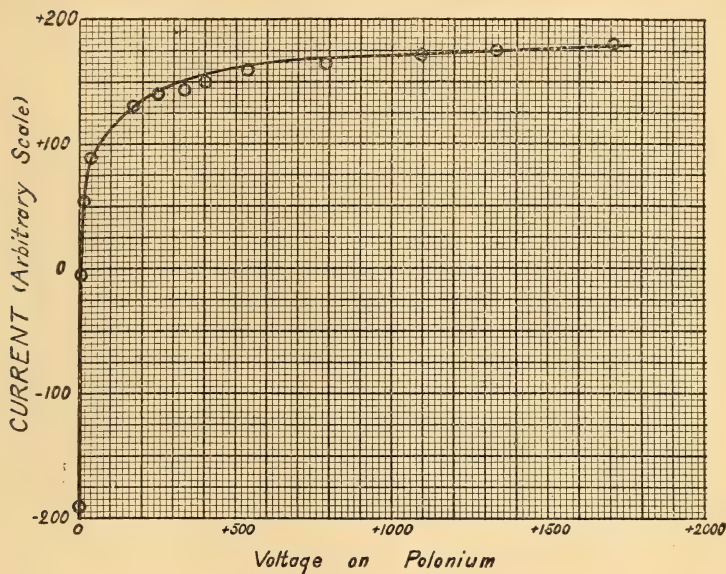
TABLE XIII.

Voltage on polonium.	Pressure of air in vessel.	Time from initial reading.	Current to electrode.
0 volts	< .001	0 minutes	-447
1.6 "	"	12 "	-191
7 "	"	16 "	-47
18 "	"	28 "	54
39 "	"	31 "	89
168 "	"	38 "	131
251 "	"	44 "	141
334 "	"	48 "	144
401 "	"	62 "	150
538 "	"	72 "	160
788 "	"	95 "	165
1095 "	"	105 "	172
1337 "	"	121 "	175
1708 "	"	137 "	181

The curve shown in fig. 8 rises very rapidly from -447 to about 90 as the potential on the polonium is increased from 0 to 40 volts, and then more slowly as the potential is increased beyond 40 volts. This is somewhat different from the results obtained in § 3 with the brass electrode and shown graphically in fig. 2, for the curve in fig. 2, it will be seen, rises rapidly while the potential on the polonium is raised from 0 to 40, and then falls again as the potential is further increased. The cause of this fall in the rate of charging of the brass electrode as the potential on the

polonium was raised above 40 volts in a measure may be attributed, as has been suggested, either to a more profuse reflexion of α rays from the electrode as the potential of the polonium was raised or to a gradual decrease in the ionization

Fig. 8.



current due to a lowering of the pressure of the air in the apparatus. But as a result of the later experiments performed with the carbon electrode, it is clear we must add another and more important cause for the fall, namely, the decrease in the secondary radiation throughout the experiment as the gas layer on the electrode became less and less dense.

The experiment just described with the carbon electrode shows that, when the gas-layer was removed, there was no fall in the rate of charging of the carbon electrode as the potential on the polonium was increased, but instead a gradual increase was obtained.

The question arose, then, whether the brass electrode would act in the same manner as the carbon electrode if the gas-layer was first removed from it. To answer this question the brass electrode was kept *in vacuo* a long time and the experiment with it was repeated. Contrary to expectation, it was found that there was still a very slight decrease in the rate of charging of the electrode after the potential of the

polonium was raised above 40 volts, but this decrease was not nearly as great as before.

The reason for the final slight difference between the behaviour of a carbon and of a brass electrode appears, then, to be due to a difference between the α ray reflecting power of carbon and brass at different voltages, the brass reflecting more α rays than the carbon as the voltage was increased. If the work done by Geiger and Marsden* on the reflexion of α rays is taken to be applicable to the present experiments, it would seem that α particles cannot be reflected in sufficient numbers to account for this difference. However, the experiments described above point definitely to the reflexion of α rays as the cause of the slight difference in the behaviour of the carbon and the brass plates under the bombardment by α rays. Moreover, it can easily be shown that with the fields used variations in the speed of the α rays amounting to 1.7 per cent. must have ensued. It is just possible that this variation might be sufficient to cause such a change in the amount of α radiation reflected from the carbon and brass electrodes as to contribute, in part at least, to the above effect. It would appear, therefore, that additional experiments should be made on the reflexion of α rays of different velocities at surfaces subjected to low gas pressures before the explanation offered above of the effect observed is set aside.

7. *Summary of Results.*

1. It has been shown that there is a secondary radiation produced when alpha rays fall on a brass or a carbon plate.

2. This secondary radiation has been proved to be in part due to the presence of gas occluded in or at the surface of the brass or carbon.

3. When this gas is being removed from the brass or carbon it is found that the secondary radiation decreases, and gives rise to an effect similar to a "fatigue" of the secondary rays.

4. This fatigue effect is found to be greater for carbon than for brass. This last result was to be expected when the fatigue effect was traced to the presence of occluded gases, since carbon is known to possess a greater capacity for occluding gases than a metal such as brass.

5. From the experiments which have been described, it will be seen that the secondary radiation emitted by a

* Geiger and Marsden, Proc. Roy. Soc. Series A, vol. lxxxii. July 31, 1909.

substance like carbon under bombardment by α rays furnishes a new means of investigating the process by which gases are occluded in carbon, and probably also in other substances.

In conclusion, I wish to express my gratitude to Profesor McLennan for his suggestions and help throughout the course of this investigation.

Physical Laboratory,
University of Toronto.

LXXIX. *Ionization by Collision in Helium.* By E. W. B. GILL, M.A., B.Sc., *Fellow of Merton College, Oxford,* and F. B. PIDDUCK, M.A., *Fellow of Queen's College, Oxford* *.

THE theory of the ionization of gases by collision, due to Professor J. S. Townsend, has been experimentally verified for a large number of gases †, among them being helium ‡. In the first experiments made by the authors with helium, the gas was not quite pure (probably about 2 per cent. of impurity being present) and there was good reason for supposing that these slight traces of impurity exercised a very considerable effect upon the ionizing powers of the ions. A few experiments were performed at the time, after the gas had been purified by pumping into a chamber containing charcoal and immersed in liquid air. The supply of liquid air was then limited and only a few results were obtained, but they were sufficient to show that the impurities exercised an effect which was very large in comparison with the amount present.

The ionizing powers of both negative and positive ions, especially the latter, were increased, and as a necessary result the minimum sparking potential was lowered. It was actually reduced from 232 volts to 203, and it was conjectured that for absolutely pure gas it would be not lower than 190 volts.

A continuous supply of liquid air having since become available, the experiments were repeated and have shown that with careful purification the ionizing powers of the ions are increased even more than was thought possible; for example, the minimum sparking potential was found to be about 160 volts instead of the 190 volts conjectured.

Before giving other results and the experimental methods

* Communicated by Prof. J. S. Townsend.

† J. S. Townsend, 'Theory of Ionization of Gases by Collision.'

‡ Phil. Mag. [6] vol. xvi. 1908, p. 280.

used, it will be useful to indicate the usual way of estimating the efficacy of the ions in producing new ions by collision with the uncharged molecules of a gas.

If n_0 ions are set free at the surface of one of two parallel plates, and an electric force of X volts per cm. is applied, the number of ions reaching the other plate exceeds n_0 owing to the formation of fresh ions by collisions in the space between the plates. If on the average each negative ion creates α new ions of each sort per centimetre, and each positive ion β , the number n reaching the other plate is given by

$$n = n_0 \frac{(\alpha - \beta)e^{(\alpha - \beta)d}}{\alpha - \beta e^{(\alpha - \beta)d}},$$

where d is the distance between the plates.

It is perhaps unnecessary to state that the distance d between the plates must be long compared with the mean free path of the ions.

This formula gives at once a method for estimating α and β experimentally; for if the plates are put at three different distances d_1, d_2, d_3 with corresponding potential-differences Xd_1, Xd_2, Xd_3 , and n_1, n_2, n_3 are the numbers of ions arriving at the positive plate [n_0 being in each case the same], then α and β may be determined from the observed ratios n_2/n_1 and n_3/n_2 .

If more distances be taken, the fact that any three readings give the same values of α and β affords a test of the truth of the theory.

The values α and β having been found, there are, however, other methods of testing the theory.

Evidently α and β depend both upon the electric force X and upon the pressure p ; and it may be proved that α/p and β/p must be functions of X/p . It is usual to draw curves with X/p as abscissa, and $\alpha/p, \beta/p$ as ordinates, and it is found that the points in one figure all lie on one curve, showing that the functional relation is satisfied.

The most effective test, however, is obtained by calculating the distance between the plates for which sparking is to be expected for the given electric force, for if the plates are at a distance a apart given by $\alpha - \beta e^{(\alpha - \beta)a} = 0$, the formula shows that the number of ions reaching the electrodes is infinitely great compared with the number originally generated, so that a spark will pass. It may be further shown that this sparking potential aX is a function of pa only, and it is usual to plot Xa against pa .

The Electrical Measurements.

The experimental arrangements are shown in the figure. The parallel plate electrodes were contained in a glass bell-jar, and negative ions were set free initially by the incidence of ultra-violet light on the top plate. The metal base had a hole bored in it covered by a quartz plate, through which the light entered. The upper plate, of zinc, was fixed to a micrometer-screw which could be turned from the outside, and by means of which the plates could be put accurately at any desired distance apart, from 1 to 11 mm. The lower plate, also of zinc, had holes cut in it through which the light might pass, and was attached to the top part of the apparatus by four ebonite pillars. To improve the insulation these pillars were encircled about halfway up by tinfoil connected to earth. The upper plate was insulated from the turning-handle by ebonite and connected to the electrometer ; the lower plate was connected to the base, which in turn could be put to any desired potential by connecting to a battery of small storage-cells.

The wires leading to the upper plate and to the tinfoil over the ebonite pillars were taken out of the jar through two ebonite plugs fixed to the glass.

The joints were made air-tight with a plastic cement, while the turning-handle passed out through a tightly fitting brass collar made to fit the top of the bell-jar and rendered air-tight by being covered on top with vaseline.

The ultra-violet light was produced by a spark-gap in a leyden-jar circuit, and the method of experiment was to turn on the coil for 20 seconds and measure the resulting current through the gas by means of the electrometer and an electrostatic induction-balance *.

The Purification of the Gas.

As the effects of purifying the gas are considerable, it will be well to explain the methods adopted for getting the gas as pure as possible, and to discuss the impurities necessarily present owing to the form of the apparatus.

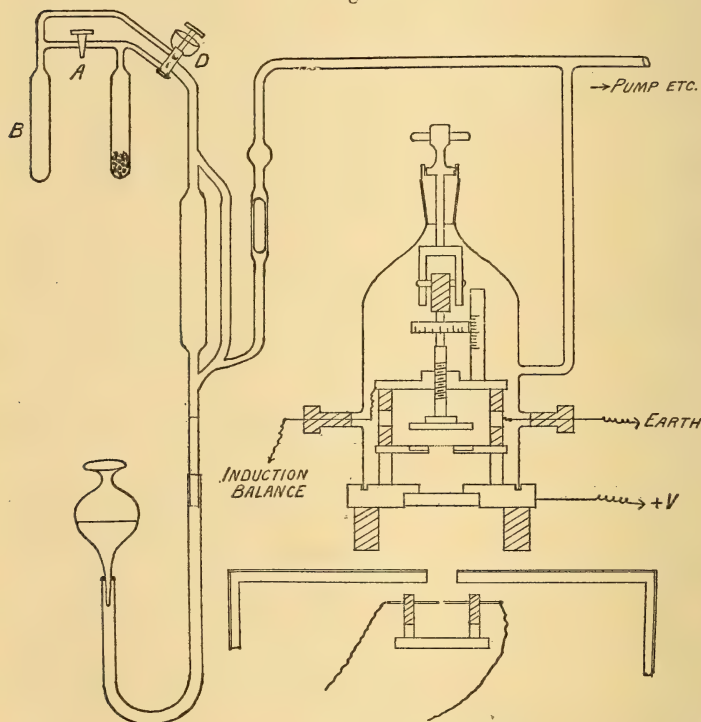
The helium, which was very kindly given to us by Sir William Ramsay, was kept in the left of the two chambers shown in the diagram [B], being always pumped there at the conclusion of an experiment. The right-hand chamber was reserved for the purification and contained coconut charcoal from which moisture and other occluded

* J. S. Townsend, *Phil. Mag.* [6] vol. vi. 1903, p. 598.

gases had been previously driven by heating to about 250° in a vacuum and pumping off the gases set free.

The mercury pump, shown in conjunction with the three-way tap D, could transfer the gas from the apparatus or

Fig. 1.



the storage-chamber to the charcoal chamber. A tap A was also inserted for convenience. In all cases the charcoal chamber was first of all surrounded by liquid air and left for some time in order that the charcoal might reabsorb any gases which might have been evolved from it since the previous purification. The tap D was then opened connecting to the apparatus, so that any impurities present there might be absorbed. Finally the helium was admitted to the cold chamber a little at a time, so that the pressure was low, and after being there for an interval was allowed to enter the apparatus by again opening D. It was then pumped back again to B and the process repeated. The effect of each washing out of the apparatus with pure helium was to reduce very much the amount of any impurity which had not been already taken out.

The helium upon which the experiments were eventually made was kept in the purification chamber for a considerable time. There is no doubt that the helium was rendered very pure by this process, a fact which was confirmed by spectroscopic observation.

The impurities due to the form of the apparatus will now be discussed :—In the first place a reference to the figure will show that mercury vapour from the pumps and gauge must be present in the bell-jar; but the amount, owing to the low vapour-pressure of mercury, is certainly small, and an experiment was made in which the gas entered the bell-jar through an additional charcoal tube in liquid air of the U-form inserted between the bell-jar and the parts of the apparatus containing mercury. The vapour was thus unable to reach the bell-jar, but no variation in the results obtained previously without this precaution could be detected. The effect of the mercury vapour seems therefore inappreciable.

Secondly, the apparatus was not quite (though very nearly) air-tight. The leak, which was tested over about a month, was uniform and caused a rise in pressure of $\frac{1}{80}$ mm. of mercury a day. An experiment to find α and β took usually a little less than an hour, and therefore the pressure of the impurity present at the end of such a set was about $\frac{1}{2000}$ mm.; the lowest pressure of helium in an experiment was 1.5 mm., and therefore the maximum impurity present was not more than .03 per cent.

In addition there were present vapours given off by the cement and vaseline used in the bell-jar. From the account given of the electrical arrangements it appears impossible to eliminate these; for instance, a quartz window had to be affixed and the various connecting wires had to be taken out of the jar. It is probable that these impurities are very small; the apparatus was exhausted for about six weeks before the helium was admitted, so that the more volatile gases would probably all have been given off; and certainly any residue was not enough to show on the McLeod gauge, which was read to $\frac{1}{400}$ mm.

Finally it was necessary to eliminate impurities given off from the plates and the glass by the electric discharge; the small currents in the gas of the order which affect an electrometer do not cause any trouble, but sparking at once brings off gases from the electrodes and the glass, and after a spark had been passed no observation was ever taken till the helium had again been purified. The electrodes were prepared by sparking between them for a very long time at a low pressure before the helium was admitted to the apparatus at all.

Numerical results obtained.

The results of the experiments for the determination of α and β are exhibited in the following tables. The distances d are given in cms., the electric force X in volts per cm., the currents (in arbitrary units) measured as the mean of several observations are given as q , while the calculated values of the current n are given in the last row, the values of α and β , from which they are derived, being shown also in each table. The agreement between the observed and calculated values q and n will be noticed.

TABLE I.—Pressure 5·2 mm.

d	·2	·4	·6	·7	·8
$X=198$ q	2·96	9·65	36·9	95	1620
$\alpha=5·44$ } n	2·99	9·45	36·5	95	1710
$\beta=.07$ }					

TABLE II.—Pressure 5 mm.

d	·2	·4	·6	·7
$X=200$ q	2·98	9·40	35·6	111
$\alpha=5·40$ } n	2·98	9·40	38	108
$\beta=.082$ }				

TABLE III.—Pressure 3 mm.

d	·4	·5	·6
$X=240$ q	10·5	20·6	55·1
$\alpha=5·5$ } n	10·4	21·4	55·3
$\beta=.12$ }			

TABLE IV.—Pressure 2 mm.

d	·2	·4	·6	·7
X=240 q	2·40	5·89	17·1	38·7
$\alpha=4\cdot2$ } n $\beta=.14$ }	2·37	5·88	18·0	39·0

TABLE V.—Pressure 1 mm.

d	·4	·6	·7	·8	·9	1·0
X=200 q	3·1	4·9	6·4	9·0	12·7	20·4
$\alpha=2\cdot37$ } n $\beta=.165$ }	2·6	4·6	6·4	9·0	13·2	22·5

The preceding tables give results from which both α and β can be calculated with accuracy ; but for the low values of $\frac{X}{p}$ β becomes very small, and in the following table only α has been found. The value of α can be found from the fact

TABLE VI.

d	·4	·6	·8	d .
Pressure 8 mm. X= 80	2·4	3·6	6·1	2·20
X=160	6·7	17·5	49	4·77
Pressure 10 mm. X=200	9·4	35·7	...	5·60
Pressure 25 mm. X=125	6·7	12·7	...	3·18
X=250	72	295	...	7·13

that for small values of β the general equation for the current reduces to $n=n_0e^{\alpha d}$. The currents for two distances are

sufficient to find α , and in general only these two readings were taken. If more are taken there is verification, but it has not been thought necessary to show this agreement for these cases as in tables I. to V.

The values of α are given in the last column, the currents from which they are obtained being in the same row.

Fig. 2.

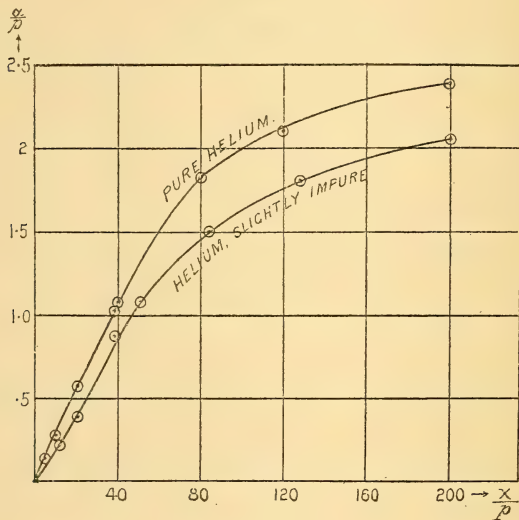
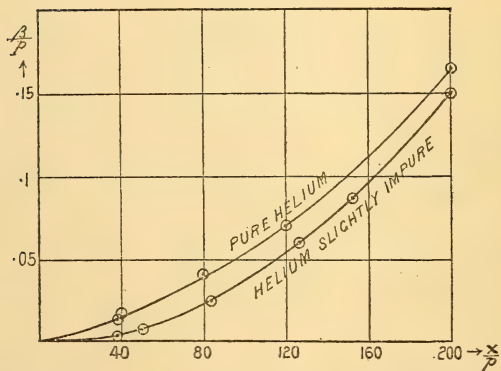


Fig. 3.



The values of $\frac{\alpha}{p}$ and $\frac{\beta}{p}$ are plotted against $\frac{X}{p}$ in figs. 2 and 3, and it will be seen that the points lie on a continuous curve, proving that the functional relations between $\frac{\alpha}{p}$, $\frac{\beta}{p}$, and $\frac{X}{p}$ are satisfied.

The values obtained are exhibited in the following table :—

TABLE VII.

$\frac{X}{p}$	$\frac{\alpha}{p}$	$\frac{\beta}{p}$
5	·126	
10	·27	
20	·57	
38	1·03	·0135
40	1·08	·0164
80	1·83	·040
120	2·1	·070
200	2·37	·165

The curves obtained in 1908 for helium with an estimated impurity of about 2 per cent. are also put in the figs. 2 and 3, showing that both α and β are diminished by a trace of impurity.

The Sparking Potentials.

The values of α and β given above determine the sparking distance a for the various pressures and electric forces from the formula $\alpha - \beta e^{(\alpha - \beta)a} = 0$. This was verified by gradually increasing the distance between the plates, keeping the electric force X per cm. constant; the distances a' at which the spark first appeared together with the corresponding sparking potential $a'X$ are given below, the agreement between a and a' is very good.

TABLE VIII.

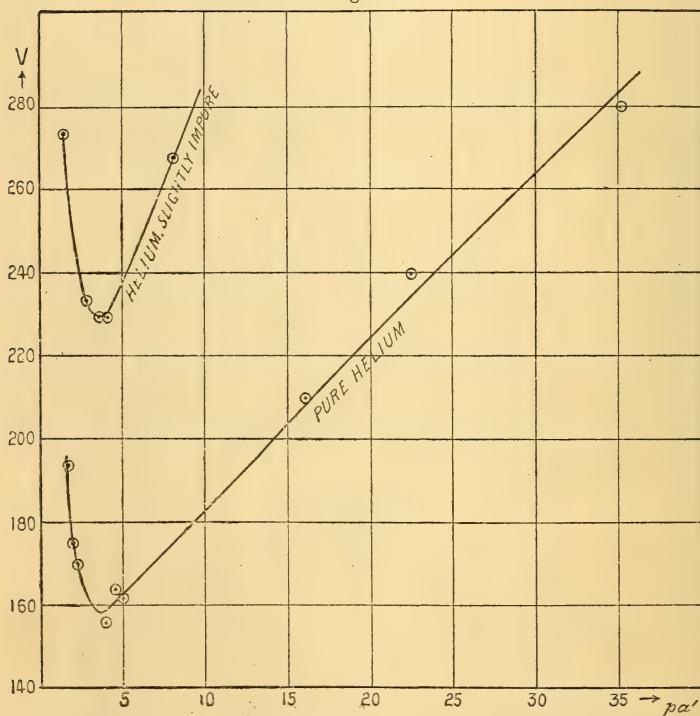
X.	p .	a .	a' .	V.
240	2	·84	·81	194
240	3	·71	·71	170
200	5	·79	·78	156
198	5·2	·82	·83	164

These sparking potentials V are plotted as usual in fig. 4 against pa' , and to get more points on the curve the following sparking potentials were also observed in the above described way, but without obtaining the values of α and β .

TABLE IX.

pa' .	V .
1.87	175
4.98	162
16	210
22.4	240
35.2	280

Fig. 4.



It will be seen that for values of p and a' such that $pa' = 4$, a discharge will pass if 156 volts are applied; and it

is necessary in consequence to take some precautions in obtaining the sparking potentials. At the higher pressures the distance from the charged plate to the earth connexion to the ebonite supports may be such that pa' is about 4, and a discharge will pass to the supports before the proper potential is reached for a discharge between the plates. To guard against this in all the above determinations (Tables VIII. and IX.) the supports were put at a potential of 75 volts.

At the lower pressures the spark would often pass round the back of the upper plate in a curved path, in the same way as in a Hittorf tube, the pa' for the curved path giving a lower value of V than the pa' for the straight path between the plates. This difficulty only occurs for values of pa' considerably less than 4, and rendered it impossible to find the sparking potential for $p=1$, $X=200$, $\alpha=2.37$, $\beta=.165$, for which the calculated pa' is 1.2.

The comparison of the results so far obtained with those obtained previously with a slightly impure gas are so striking that a set of experiments were made to find the effect upon α and β of adding known amounts of impurity. The leak of the bell-jar per day afforded a convenient method of adding known amounts of air to the helium, and the following results were obtained for the currents between the plates for different distances, the current for distance $d=.2$ being always taken as 10.

TABLE X.
Helium pressure 5 mm. $X=200$.

d	.2	.4	.6	.7	.8	.9
Pure Helium	10	31.3	119	372		
Helium with 1 in 400 air...	10	28.6	97	228	790	
„ „ 2 in 400	10	29.1	90.5	194	612	
„ „ 3 in 400	10	29.4	92.7	172	408	2410

The values of α and β were calculated from these figures and are given below, it not being thought necessary to include for comparison the currents calculated from the values, although the calculation was actually performed and the agreement found as good as those given in tables I. to V.

The sparking distances a' and the corresponding sparking potentials V are also given.

TABLE XI.

Helium. $p = 5$ mm. $X = 200$.

	α .	β .	α' .	V.
Pure Helium.....	5.4	.082	.78	156
Helium + .25 p.c. air	5.1	.069	.85	170
Helium + .5 p.c. air.....	5.0	.065	.88	176
Helium + .75 p.c. air	5.0	.051	.93	187

General Discussion of Results.

The last table shows very clearly the effect of impurities upon the ionizing powers of the ions. As far as α is concerned the effect of 3 parts in 400 of air is to reduce the value of α by about 8 per cent., but the effect upon β is very much greater, reducing it from .082 to .051, that is by nearly 40 per cent. The other two values of β are not necessarily very accurate, as they were not tested by passing a spark for fear of adding more impurities to the gas, but the value .051 was thus tested and found correct, as was the value .082 in the course of the experiments given in Table II.

A possible explanation for the fact that the impurities have a much greater effect upon the positive than upon the negative ions, is that they more readily attach themselves to the slow moving positives than to the much faster negatives; the positives thus loaded are less effective in producing fresh ions by collision, because they are longer in reaching the critical velocity necessary for ionization. Experiments upon the velocities of the positive ions in helium should give interesting results. The reduction of β makes a very great difference to the sparking potential, less than 1 per cent. of impurity bringing it from 156 to 187 volts.

The minimum sparking potential attained of 156 volts is far below that observed before for any other gas; those of nitrogen 298 volts, argon 233 volts, and hydrogen 273 volts, being the three lowest previously obtained.

A formula can be obtained for $\frac{\alpha}{p}$ in terms of $\frac{X}{p}$ by making simple assumptions as to the effects of collisions on the velocity of the ions*.

* J. S. Townsend, 'Theory of Ionization of Gases by Collision,' p. 23.

Thus, if $\frac{1}{N}$ is the mean free path for 1 mm. pressure, V the least potential difference between the ends of a path to cause a negative ion to acquire sufficient velocity to generate others by collision, then when $p=1$

$$\alpha = Ne^{-\frac{NV}{X}}.$$

The agreement of the α 's found with this formula for the values $N=2.8$, $V=12.3$, is given below.

TABLE XII.

X	200	160	120	80	40	20
α found experimentally ...	2.37	2.27	2.1	1.83	1.07	.57
$Ne^{-\frac{NV}{X}}$	2.35	2.26	2.1	1.82	1.18	.50

This value of V is also lower than for any other gas, the next, among those examined, being hydrochloric acid for which $V=16.5$ volts. For air it is 25 volts.

In conclusion, we wish to express our thanks to Prof. Townsend for valuable advice during the course of the experiment.

LXXX. *Remarks on the Production of Condensation Nuclei in Air and in Vapours by Intense Cooling and by Ultra-Violet Light.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN connexion with the paper by Mr. Gwilym Owen which appeared in the Philosophical Magazine for October, 1911, p. 563, entitled "Note on the Production of Nuclei in Air by Intense Cooling," I should like to lay before you some considerations which seem to explain the results there obtained. These considerations are based on a series of experimental researches on allied subjects which I carried out together with Professor P. Lenard*.

* P. Lenard and C. Ramsauer: "Ueber die Wirkungen sehr kurzwelligen ultravioletten Lichtes auf Gase und über eine sehr reiche Quelle dieses Lichtes." *Heidelberger Akademie*. Five Parts: I. Aug. 2, 1910; II. Nov. 5, 1910; III. Dec. 20, 1910; IV. June 9, 1911; V. Aug. 4, 1911.

Phil. Mag. S. 6. Vol. 23. No. 137. May 1912. 3 K

Our experiments were concerned with the action of ultra-violet light of very short wave-length on gases, more especially air. By means of systematic precautions in the drying and purifying of the gases, directed especially against very small impurities which, although not otherwise detectable, have here a very important influence, we succeeded in separating the different actions of the light (chemical action, formation of nuclei, formation of electrical carriers), and explaining the nature of effects due to their coexistence, which are often very complicated. The quantitative measurements were first made on the carriers of electric charge, whose size and other particulars were obtained from their velocity of wandering, determined by the cylinder condenser method. The carriers thus measured arise from the combination of larger nuclei, originally uncharged, with carriers of molecular size, so these measurements give information concerning the size, number, and formation of the nuclei themselves. The electrical measurements therefore solve the same questions as can be answered by means of Wilson's experiment, as in the work of Mr. Owen*.

It is thus possible for us to compare the results we obtained with cooling directly with those of Mr. Owen†. We observed the same facts as he did. If carefully dried air is cooled to a low temperature, uncharged nuclei are formed, which in our experiments, where the cooling was only used for purification, were removed by passage through a filter, also cooled. These nuclei, however, do not consist of aggregates of air molecules, but of condensed gases (CO_2 , NH_3 , organic vapours, last traces of H_2O) present in small quantities in the air, as follows from the fact that the formation of nuclei by means of ultra-violet light observed before no longer takes place after cooling. This formation of nuclei is, however, immediately restored if the air, after purification as above, passes over surfaces of any material, though these may be clean in the ordinary sense (for instance, a short, clean, glass tube which has not previously been glowed). This is due to the surfaces spontaneously giving off traces of vapour, which they have absorbed from the atmospheric air. Only by heating all the walls of the vessel to a dull redness, until the glass becomes soft, for instance,

* Prof. Becker has worked out in this way an electrical method of measuring the size of nuclei, by using Röntgen rays to produce the carriers of electric charge, and so avoiding the complication of formation of nuclei by the light itself.

† Lenard and Ramsauer, *loc. cit.* See especially Part III.

can we get rid of the formation of nuclei, that is, of these traces of vapour.

We may, I think, therefore assume that in Mr. Owen's experiments the nuclei consist neither of H_2O , as the preliminary drying was so extremely careful, nor of aggregates of air molecules, but of aggregates of the before-mentioned easily condensed gases and vapours, which are continuously given off spontaneously from the walls and the phosphorus pentoxide during the prolonged course of the experiment, and also especially on the alteration of pressure during the cooling, and which are formed through the action of cold into nuclei. For however careful the drying and purification may be, they do not suffice, according to our experience, to remove these constituents, as it was impossible for Mr. Owen to heat the taps, and the glass in their neighbourhood, sufficiently; the evolution of gases from the phosphorus pentoxide must also be taken into account.

Apart from these considerations, our experiments give a *direct proof* that, if the air were completely freed from the minor constituents mentioned, the phenomena could not have occurred*. We boiled off air from liquid air, and brought the current of air at once to the room temperature by passing it through a thin glass tube immersed in cold water; the vessel where the gas was subjected to the rays and all the tubes leading to it had been previously heated to $500^{\circ} C$. The air was then subjected to Schumann ultra-violet light (wave-length less than 180μ), which, according to our experiments, produces carriers of electricity in the chief gases of the atmosphere, owing to its selective absorption. With this arrangement the aggregates of air molecules observed by Mr. Owen ought certainly to have been present, as the air immediately after vaporising possesses a temperature more than sufficiently low; the aggregates ought also to have persisted during their passage to the vessel where the air is exposed to the rays, as the duration of this passage was much shorter than in Mr. Owen's experiments. The aggregates would have been detected in the measurements by the combination with carriers of electricity which always takes place. However, only carriers of about molecular size were observed, which are formed from the gas itself, and, for instance, do not have any effect on Helmholtz's steam-jet.

It is thus made certain that these molecular aggregates are not formed in very pure air, and thus that they must be formed of the minor constituents, which are always present

* Lenard and Ramsauer, *loc. cit.* See Part V.

in the air and are adsorbed at all the surfaces of the apparatus, to be afterwards slowly given up spontaneously if the surfaces are not freed from them by vigorous heating. The formation of the aggregates in Mr. Owen's experiments is thus due to easily condensed minor constituents of the air, which are first adsorbed and afterwards slowly given up by the walls and the phosphorus pentoxide, as these were not sufficiently heated.

Also with regard to another paper of Mr. Owen's (Phil. Mag. April 1911, p. 455, "On Condensation Nuclei produced by the Action of Light on Iodine Vapour"), in explanation of effects there described I should like to call attention to our experiments (P. Lenard and C. Ramsauer, *op. cit.* Part III.), where we have shown that glass-wool and every glass surface that has not been strongly heated continuously gives off adsorbed minor constituents of the air, which on the production of ozone by ultra-violet light always lead to the formation of nuclei; now, according to Mr. Owen himself, ozone is formed in his experiments. The regeneration of the effect on washing the walls with distilled water is explained by the fact that the water must contain dissolved small quantities of the vapours and gases mentioned before (for instance, NH_3), and as it trickles down give these up to the glass walls through adsorption. These observations led us to construct asbestos filters of combustion glass, which could always be cleansed by being heated to redness, while glass-wool or cotton-wool filters, which are generally used finally to free a current of purified air from dust, have just the opposite effect, and charge the air again with all the impurities which have been previously removed, thus vitiating the results. All previous work on the action of ultra-violet light on gases, and especially on the formation of nuclei in gases, suffer from this source of error.

I am, Gentlemen,

Yours faithfully,

Radiologisches Institut,
Heidelberg, 24 Nov., 1911.

CARL RAMSAUER.

LXXXI. *A Note on the Electrification of the Atmosphere and Surface of the Earth.* By W. A. DOUGLAS RUDGE, *Professor of Physics, University College, Bloemfontein* *.

IN the course of some work on the value of the atmospheric potential gradient in South Africa, the author has pointed out the important influence exerted by the clouds of dust raised by the wind. The normal fine weather charge

* Communicated by the Author.

possessed by the atmosphere is of course positive, and in Bloemfontein, at an elevation of 4500 ft., seldom exceeds a maximum value of 200 volts per metre. But during a dust storm the sign of the charge changes, and gives rise to values exceeding 500 volts per metre. It is not necessary for the instrument used for measuring the potential to be actually in the dust itself, for a "dust devil," *i.e.*, a whirlwind which carries up a column of fine sand, sometimes two or three hundred feet in height, can produce a very perceptible effect at a distance of more than two miles, reversing the positive charge in the air and giving a large negative one.

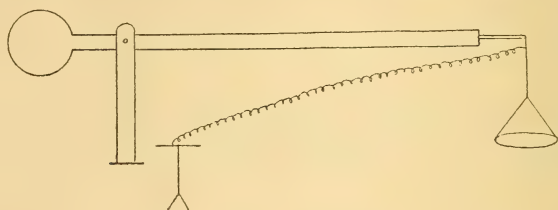
It is generally believed that as a consequence of the air-earth current flowing into the earth, the latter possesses a negative charge; an explanation of the negative potential caused by the dust storm appeared to lie in assuming that the particles of sand carried up by the wind, being themselves negatively charged, gave rise to the negative potential. But this is not the case, for, as will be shown, the dust particles are positively charged, and, at all events in the situation where the observations were carried out, the surface of the earth is also charged with positive electricity.

The climate of South Africa is, on account of its dryness, eminently suitable for observations on atmospheric electricity; but it is quite possible that similar conditions may prevail elsewhere, and the following experiments may perhaps be successful in other places.

(1) *The charge upon the Earth's Surface.*—If the earth is a charged body, it seemed that it might be possible to remove a portion of the charge, and test its magnitude and nature by an electroscope. So with this object the writer used a large proof plane, about 500 sq. cm. in area, composed of gilded wood (originally made by Sir Wm. Snow Harris for his weight electrometer) attached to a long ebonite rod; the surface of the earth and objects upon it were tested by touching for an instant, and then carrying the proof plane to an electroscope placed upon a step-ladder at a height of 2 metres above the ground. When this was done the proof plane was found to have a *positive* charge in all cases. The magnitude of the charge, however, depended upon the nature of the material with which the proof plane had been in contact, the most satisfactory surface being that of the firmly compacted soil.

The method of conducting the experiment was then modified, so that the observer could take observations without leaving the electroscope.

A long light rod of wood was balanced upon a pivot. To the end of the wooden rod an ebonite one was attached, and from this there was suspended an aluminium plate about $\frac{1}{8}$ sq. metre in area, and from this a fine wire was taken to



the electroscope. By tilting the counterpoised end of the rod, the plate could be put in contact with the earth, then quickly raised to a height of about 4 metres above it, any charge removed from the earth being indicated by the electroscope. By this means it was shown that the surface of the ground did possess a positive charge which, although small, was quite definite.

If a block of insulating material (even dry wood will answer in this climate) was placed so that the plate rested in contact with it, but did not touch the ground, then no charge was obtained, and only a small charge if a block of dolerite was used, but coating the wood with tinfoil allowed of a charge being obtained.

It must be pointed out that these experiments were carried out in dry weather when the earth's surface was very poorly conducting. It is quite conceivable that in wet weather a different result might have been shown; but under the conditions of the experiment there certainly was a definite charge of positive electricity. In order to prevent the possibility of there being any electrification due to friction between the plate and the earth, a small spiral spring was attached to the plate, so that it could make contact with the earth without rubbing against it.

(2) *The charge upon the Dust carried up by the Wind.*—In order to collect the charge in the air, a plate coated with radium was attached to the electrometer. Various means were adopted by which a cloud of dust could be raised, such as throwing a handful of dust into the air; by directing a stream of air from a pair of bellows against a heap of fine dust; by shaking from the end of a pole a fine muslin bag filled with fine dry sandy earth; and lastly, and most efficaciously, by setting a team of mules to plough up the dry

earth. In all these cases, an electroscope placed at some little distance from the cloud gave indications of a negative charge being present in the air. This could be detected by the normal positive charge indicated by the electroscope becoming smaller, or if the distance was less than 50 metres the charge would be reversed and potentials up to 200 volts per metre registered.

In the course of these experiments, it was noticed that if the dust fell upon the electroscope the effect was smaller, as though the dust had imparted a charge of a character different from that given by the air, and further investigation showed this to be the case. The charge upon the dust was always positive. This was easily shown by taking a conical net of fine wire gauze, drawing it rapidly through the cloud so as to catch some of the dust raised by the plough, and then putting it in communication with the electroscope, when a very strong charge of positive electricity was shown, and on some occasions small sparks were drawn from the net.

The negative charge indicated by the electroscope during a dust storm must thus reside in the air itself, and not in the dust particles caught up by the wind. By way of contrast, it may be noted that when steam suffers condensation in the open air, it gives to the air a positive charge which persists after the cloud has disappeared. The general electrification produced by raising dust composed of different materials has been investigated, and will form the subject of a future paper.

Note added April 3rd.

During a journey from South Africa to Europe observations were taken as occasion offered, and the following may be of interest.

On March 7th the normal electrification of the atmosphere near Cairo was positive, and at 7 A.M. of the order of 150 volts per metre. On following in the track of a caravan of camels near the Pyramids the potential varied from zero to 50 volts per metre *negative*. On March 14th, at Pozzuoli near Naples, the potential gradient at sea-level was 80 volts per metre and positive. On ascending to the summit of the Solfatara, the potential fell to zero owing to the action of the steam-jets issuing from the volcano, but on stirring up the fine volcanic dust lying round the vents, a cloud was raised and this caused a *negative* potential gradient reaching to 100 volts per metre.

LXXXII. *Theory of Ionization by Collision.**To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

IN a paper on the theory of ionization by collision, published in the March number of the *Philosophical Magazine*, Mr. Campbell criticises my work on that subject, and explains what he imagines is the basis on which the theory depends. I would like to point out a few facts in connexion with that subject, and also to make some remarks on the following statements which appear among his conclusions:—

1. With regard to my assumption that the negative ion does not undergo any permanent change in its properties as a consequence of repeated collisions, "This assumption is contradictory to the older view of ionization by collision, according to which the negative ion when first formed is an electron, but subsequently becomes a complex ion by gathering round it neutral molecules."

2. The mathematical argument is sketched, and it is pointed out that it contains an error.

With regard to the older views of the theory, as they appeared in print, I think Mr. Campbell will find he is mistaken. I have always held the same view with regard to the electronic state of the negative ion when ionization by collision is taking place. As far as I can find, the first paper in which ionization by collision is mentioned as providing a solution of any electrical problem is that which I published in '*Nature*,' August 9, 1900, describing the results obtained with negative ions produced by Röntgen rays. A more detailed examination was made of those experiments in the paper in the *Philosophical Magazine*, Feb. 1901, in which it was shown that if the negative ions generate others at a rate α per centimetre under a force X in a gas at pressure p , the three variables must be connected by an equation of the form $\frac{\alpha}{p} = f\left(\frac{X}{p}\right)$, the hypothesis being that the negative ions act as ionizing agents throughout the whole time they are in the gas, and that the positive ions are comparatively inactive. The experiments are not so accurate as those made with ultra-violet light, not because of the mathematical difficulty of expressing the currents, but because the initial distribution of the ions in the gas is unknown. They were quoted in my book to which Mr. Campbell refers as showing that the negative ions generated by Röntgen rays from the molecules of any gas are all the same, being small compared with the molecule of hydrogen, and identical with the ions set free from a metal surface by ultra-violet light. This fact is of

importance, and I do not know of any previous experiments which show that the negative ions generated by Röntgen rays from molecules are electrons and not atoms.

The view that negative electrons combine with molecules or form groups of molecules when the electric force is so great that ionization by collision takes place, is a contribution to the theory which was subsequently made by Professor Sir J. J. Thomson in a paper that appeared in the *Philosophical Magazine*, April 1901. I do not know what experimental evidence there is in favour of it, but I did not neglect to consider it, as Mr. Campbell implies. In my book on the subject of *Ionization by Collision*, I dealt with the matter and mentioned two reasons against that hypothesis. One, which is explained in the latter portion of the book, was based on some accurate determinations of currents between parallel plates when negative ions were produced by collisions; the other was based on experiments on the motion of negative ions when forces much smaller than those required to generate ions by collisions were acting. On the latter subject the reader was referred to some papers published in the 'Proceedings' of the Royal Society.

Perhaps I may mention some values I have recently obtained for the rates of diffusion of negative ions into air at various pressures, as they illustrate the substance of the second argument.

The coefficient of diffusion is not independent of the electric force. When a small force 1.5 volts per centimetre is acting the coefficients of diffusion of the negative ions into air are .045, .54, and 33000, at pressures 760 millimetres, 16.5 millimetres, and 4.5 millimetres respectively.

The number corresponding to the pressure 4.5 was obtained with ions that had made on an average 8000 collisions with molecules of air before their motion was investigated. If there was any tendency for the ions to become attached to molecules they had ample opportunity of doing so, and their rate of diffusion would then have been smaller than the rate of diffusion of hydrogen molecules.

The rate of diffusion of hydrogen into air at 4.5 millimetres pressure is about 105. This number differs considerably from 33000, which shows that, even after making 8000 collisions with molecules, the large majority of the ions must be in the electronic state at any time. If this state persists to such an extent when a low force 1.5 volts per centimetre is acting, it is more than likely that it should persist to a greater extent under such forces as are sufficiently large to produce ionization by collision.

The second conclusion as to the erroneous nature of the mathematical work is, as far as I can gather, to be found in

the equations for currents between parallel plates and in the method of representing a certain curve obtained experimentally by a mathematical formula.

The most accurate experiments, namely, those with ultra-violet light, from which all the numbers given in the tables and curves were deduced, are as follows. When ions start from one plate and travel towards another parallel plate at distances $x_1, x_2, \&c.$, from the first plate, the numbers $n_1, n_2, \&c.$, that arrive at the second plate are given accurately by the formula $n = n_0 \epsilon^{\alpha x}$. This is exactly what would be expected from the theory on the assumption that on an average a negative ion moving under a constant force generates α ions per centimetre of the gas. As in all experiments in which a mean constant velocity is attained in a resisting medium, the first distance must be sufficiently great to allow the ions to assume that velocity. No experiments were made at short distances, or with small potential differences between the electrodes of the order of 20 or 30 volts. It is not necessary to specify the mean velocity more particularly than to define it as the mean velocity of the ions after those that are initially started have traversed several free paths. In the mean velocity obviously it is necessary to reckon the velocities of ions that have just been generated. Under these conditions the mean velocity of ions traversing planes at distances $x_1, x_2, \&c.$ from the plane $x=0$ will all be the same, and mathematically it is correct to say that the numbers arriving at those distances are given by the equation $n = n_0 \epsilon^{\alpha x}$.

Mr. Campbell wishes for a formula that would apply to distances so short that the final mean velocity would not be attained in it. I cannot see of what use it would be in these experiments. The expression $n = n_0 \epsilon^{\alpha x}$ appears to be no more erroneous for the values of x that have been used than the expression M/r^2 for the force outside a spherical distribution of attracting matter, which does not hold when r becomes smaller than the distance of the outer layers from the centre.

The most important step in establishing the theory is to show that the experimental results satisfy the relation $\frac{\alpha}{p} = f\left(\frac{X}{p}\right)$. The theory requires that this formula should hold between the variables, and it has been found to be satisfied accurately.

Mr. Campbell seems to think that the basis of the theory depends on being able to express the function f accurately by means of a mathematical formula. This is where his criticism is most at fault. In order to obtain any formula to express this function it is necessary to make many

assumptions, none of which are required by the theory. We have no knowledge as to the exact effect of a collision on the velocity of an ion when the velocities are very large, and the probability of guessing the correct assumptions is very small indeed. Under these conditions one selects that expression for the velocities which gives the simplest formula for the curve. As it happens, a very simple formula, agreeing accurately with the larger values of α , can be obtained. In one respect it is unfortunate perhaps that the formula which I gave does agree with the curves so accurately, as it has led some people to think that it is an integral part of the basis of the theory. As a matter of fact, several such expressions for α may be found which do not differ from the observed numbers by quantities greater than the experimental errors, and it is therefore impossible to decide from the experiments which are the most correct.

The maximum value of α is of the same order as obtained from many of the formulæ, so that possibly the values of N that have been found are correct within 10 per cent.

The subsequent deductions that can be made from the numbers given for N , as to the sizes of molecules, involve further uncertainties. Thus it is assumed, for instance, that the velocity of agitation of the ions may be neglected. It may be shown experimentally that as the force increases the velocity of agitation of the ions increases abnormally, and the sum of the paths traversed by an ion in going one centimetre in the direction of the force may be appreciably greater than one centimetre. On this account the values obtained for the diameters of the molecules are probably not as correct as the determination of the maximum values of N .

Mr. Campbell states that his estimates of the diameters of molecules are nearer those obtained by the theory of viscosity, than the estimates which I gave. It should be remembered, however, that the value obtained for the diameter of a molecule depends on the specification of a collision, and a collision as defined by this theory is not the same as a collision as defined in the ordinary theory of viscosity. The diameter of the molecules obtained by the different methods are not necessarily the same. Mr. Campbell's statements appear therefore to be incorrect as regards any matter that is of importance in connexion with the theory of ionization by collision. With regard to other matters, such as the diameters of molecules, his conclusions must be very uncertain. They depend on the validity of his assumptions as to the effects of various kinds of collisions on the velocity of the ions, and there is no evidence to show that his hypotheses are correct.

Yours truly,

JOHN S. TOWNSEND.

LXXXIII. *On the Trisection of an Angle.**To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

IN Mr. Maskelyne's figure (Phil. Mag. April, p. 647)
let

$$ag = x, \quad ah = y,$$

$$bac = \alpha, \quad baj = \theta.$$

Then

$$aj = y = \frac{3}{2}x \cos \frac{\alpha}{2},$$

and

$$\frac{\sin \alpha}{2 - \cos \alpha} = \tan adg = \frac{y \sin \theta}{2x - y \cos \theta},$$

so that the equation to determine θ is

$$6 \sin \theta + 3 \sin (\alpha - \theta) - 8 \sin \frac{\alpha}{2} = 0,$$

which is not satisfied by $\theta = \frac{\alpha}{3}$.Let $\alpha = 6\beta$, $\theta = 2\beta + \epsilon$.Then if β is small,

$$\epsilon = \frac{4}{3}\beta^3 - \dots,$$

which gives an approximation to the error.

So possibly the eminent men are right.

Yours faithfully,

Newnham College, Cambridge,
April 1912.

HILDA P. HUDSON.

LXXXIV. *On the Trisection of an Angle.**To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

1 Selwyn Gardens, Cambridge,
16th April, 1912.

IT seems unnecessary to give any formal proof that Mr. Maskelyne's construction (Phil. Mag. April 1912, p. 646) cannot trisect an angle with exactness; but it may be of some interest to estimate the degree of accuracy in his approximation.

For a small angle the error seems to be of the order of the cube of the angle; thus an angle $3a$ is divided by this method into parts which are approximately $a + \frac{1}{6}a^3$, $a - \frac{1}{3}a^3$, $a + \frac{1}{6}a^3$,

if a is small. For larger angles, numerical calculation is the only process available. The accompanying table gives the parts into which the angles entered in the first column are divided by the construction; the results are given in degrees and decimals, of which the last figure is only approximate.

30	10°05	9°90	10°05
60	20°33	19°34	20°33
90	30°95	28°10	30°95
120	41°68	36°64	41°68
150	52°43	45°14	52°43

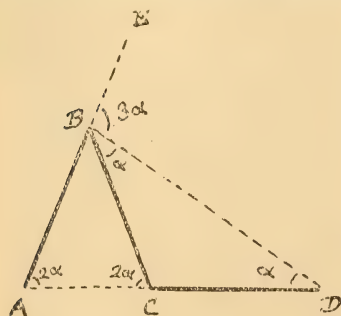
It will be seen that the error appears to increase with the angle, being about a degree for an angle of 90° , and nearly $2\frac{1}{2}$ degrees for an angle of 150° .

Yours faithfully,
T. J. P^A. BROMWICH.

LXXXV. *Note on the Trisection of an Angle.*

By J. R. COTTER, M.A.*

WITH reference to the point raised by Mr. Maskelyne in the last issue of the Philosophical Magazine, viz., the mechanical trisection of an angle, the following device is perhaps the simplest that can be suggested.



AB, BC, CD are three equal rods jointed at B and C. If A lies on CD or on CD produced (as in the figure), and if the angle BDC is α , then the other angles have the values given in the figure, since ABC and BCD are isosceles triangles. If then we make the point A slide on CD produced, till the exterior angle DBE has a given value, the angle BDC will give the required third part.

This method does not of course claim to be a "rule and compass" method.

* Communicated by the Author.

LXXXVI. *Notices respecting New Books.*

Some Problems of Geodynamics. By A. F. H. LOVE, M.A., D.Sc., F.R.S. Cambridge University Press. 1911.

The Tides and Kindred Phenomena of the Solar System. By Sir GEORGE HOWARD DARWIN, K.C.B. Third Edition. London: John Murray, 1911.

PROFESSOR LOVE's Essay was awarded the Adams Prize in the University of Cambridge in 1911. It is a mathematical treatise which discusses the origin and nature of the various stresses which exist in the interior of the earth. The problems attacked and the main conclusions reached are given in non-mathematical form in an introductory Abstract of 17 pages; and in most of the chapters the average reader will find pastures of easy English on which to feed his scientific curiosity.

Differing in form and yet treating in part of some of the same problems, Sir George Darwin's book on the Tides, originally published in 1898, is now issued in its Third Edition. The kindred phenomena spoken of in the secondary title include discussions of Saturn's Rings and Satellite systems in general, of the origin of spiral nebulae and double stars, and in fact the evolution of the cosmos. Tidal action in the true Newtonian sense of the term is the never ceasing agency which brings about the wonderful variety of configuration of stellar systems distributed through space.

The most important of the problems discussed by both authors is the tidal deformation of the earth's crust, the existence of which was first demonstrated a few years ago by Dr. Hecker of Potsdam, now of Strassburg. The search for this yielding of the earth as a whole to the tidal action of sun and moon was initiated in 1863 by Lord Kelvin, then William Thomson; but it was not till the lapse of 44 years of strenuous endeavour on the part of several independent investigators that a definite result was gained. An unlooked-for lack of symmetry in the amount of yield of the earth's crust is made the subject of a special investigation by Professor Love; and following his suggestions the International Seismological Association have determined to instal suitable instruments in variously situated localities near to and far from the ocean.

Among other interesting questions, Professor Love works out the problems of gravitational instability, first expounded by Jeans, and concludes his essay with a thorough discussion of the vibrations of a gravitating compressible planet and the propagation of seismic waves through the mass or over the surface. One general conclusion of all this recent research is thus put by Sir George Darwin: "Although there are still some—principally amongst geologists—who believe in the existence of liquid matter under the solid crust of the earth, yet the arguments which I have sketched appear to most men of science conclusive against such belief."

Both authors are to be congratulated upon the lucidity of their expositions of difficult problems, towards the solution of which they have each made valuable contributions. Professor Love's mathematical presentation of the subject is elegant and powerful, the fundamental assumptions being clearly laid down, and the interpretations of the formulæ fully given. It is a model for all future investigations along these lines.

A Treatise on Dynamics, with Examples and Exercises. By ANDREW GRAY, LL.D., F.R.S., and JAMES GORDON GRAY, D.Sc. Macmillan & Co. Limited. London, 1911.

Analytical Mechanics, comprising the Kinetics and Statics of Solids and Fluids. By EDWIN H. BARTON, D.Sc., etc. Longmans, Green & Co. London, 1911.

No student aiming at higher work in Physics, Engineering, and Astronomy, can afford to neglect the thorough study of dynamical science. To meet the needs of such students, Professor Gray of Glasgow and Professor Barton of Nottingham have almost simultaneously prepared and published the treatises named above. It may be said at once that the three authors (for Professor Gray has his son as collaborator) are to be congratulated on the excellent manner in which they have done their work. Whichever book the student takes as his guide he will be well led. Professor Barton says that his "work is not written to any one examination syllabus." Yet it is a pity that he should have emphasised the examination system as an end-all by the explicit mention of the examination papers from which he has culled many of the examples. Most of those labeled "Lond. B.Sc." do not differ essentially from old familiar friends who first saw the light in the Cambridge Senate House perhaps a generation ago. Very rarely has the examiner on the intermediate standard produced a real original question during the last ten years. What is here protested against is not the inclusion of the question as a valuable exercise for the student, but the addition *in capitals* of a certain examination it figured in, thereby tending to emphasise unduly in the students' eyes this least satisfactory part of our educational methods.

The distinctive features of the books may be indicated by the following comparisons. Professor Barton takes a wider sweep over the dynamics of solids and fluids, discussing for example the simpler problems of hydrodynamics and elasticity. Professor Gray limits himself to particles and rigid solids and the statics of flexible strings, omitting even Attractions and Potential; but he carries the discussion into higher fields. Both authors devote a chapter to gyroscopic motions; but here again, as was to be expected in one who had been trained under Kelvin, Professor Gray enters much more fully into the many problems which illustrate what Maxwell called 'gyrostatic domination.' Professor Barton gives an interesting sketch of the recent attempts to

substitute for Newton's Laws of Motion a more logical series of enunciations. Professor Gray makes not the least reference to these discussions. He explains simply the meanings of the Laws, and in his seventh chapter gives a remarkable and original series of applications of the principles to such practical questions as the efficiency of brakes, the dynamics of self-propelled vehicles, the effect of small periodic variations on the motion of a carriage or ship, etc. In his chapter on general dynamical methods, Professor Gray develops the methods associated with the names of Lagrange, Hamilton, Jacobi, Kelvin, Bertrand, and others, giving a clear account of the distinction between holonomous and not holonomous systems. By restricting himself to the more elementary modes of treatment, Professor Barton gains space for more detailed study of the statics of rigid bodies, which will commend the book more especially to engineering students. He has also a chapter on mechanisms. These remarks may suffice to show that, although they have much in common, the books are markedly distinct. Each has its merits; and when due regard is paid to the aims of the authors the demerits, if there be any, are negligible.

RECENT publications of the U.S. Coast and Geodetic Survey include:—

- (a) *Distribution of the Magnetic Declination in the United States for January 1, 1910.*
- (b) *Results of Observations made at the...Magnetic Observatory at Vieques, Porto Rico, 1907 and 1908.*
- (c) *Results of Observations made at the...Magnetic Observatory at Baldwin, Kans., 1907-09.*
- (d) *Results of Magnetic Observations made...between July 1, 1910, and June 30, 1911.*

In (a) there is a large size declination chart, showing the isogonals (lines of equal declination) and lines of equal rates of secular change for the epoch considered. There are also particulars of secular change for previous epochs at a number of stations.

The records of magnetic observations—diurnal inequalities, copies of magnetic storms, etc.—in (b) and (c) follow the same lines as in previous years. The most notable special events which they chronicle are that the Vieques Observatory has been moved to new quarters at a small distance from the original ones, and that the Baldwin Observatory has been discontinued and the instruments transferred to a new observatory at Tucson, Arizona. (d) gives particulars of a year's field work carried out by the magnetic observers of the American Survey. The land stations occupied numbered 351, about a quarter being "repeat" stations, used for the determination of secular change. The positions of the stations are described, as well as the results of the observations at each. At sea the observations taken by the surveying vessels numbered 35, the majority being taken on the Pacific Ocean.

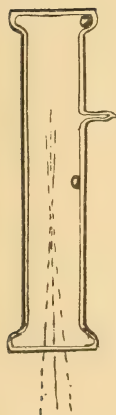


FIG. 1.



FIG. 2.



FIG. 3.

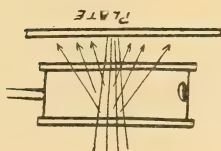


FIG. 5.

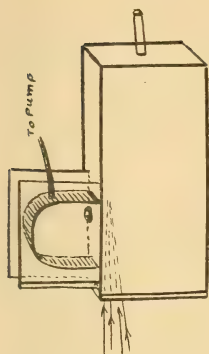


FIG. 6.

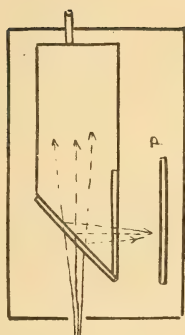


FIG. 7.

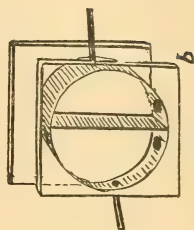


FIG. 4.

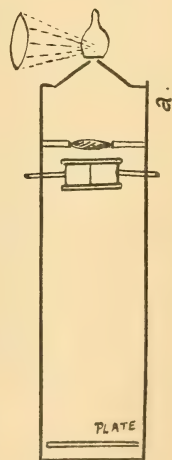


FIG. 4.

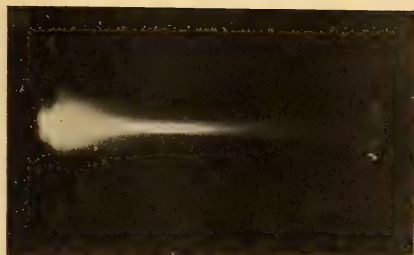


FIG. 1.

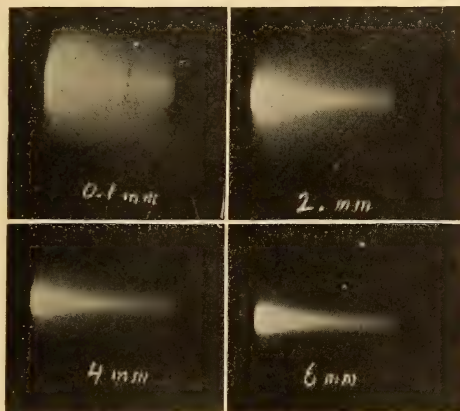


FIG. 4.

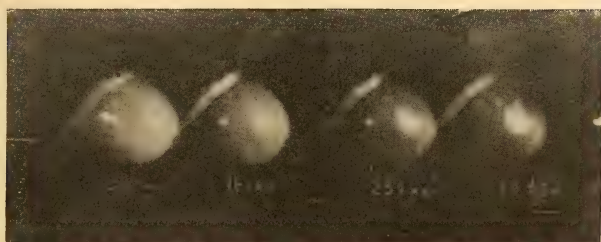


FIG. 6.

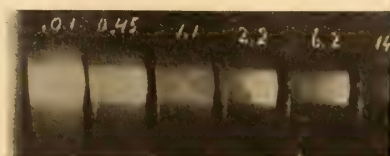
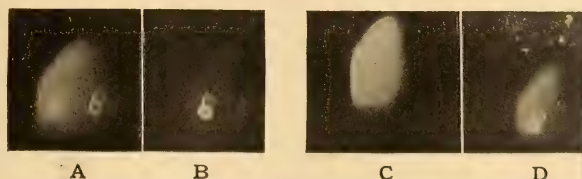


FIG. 12.



FIG. 1.

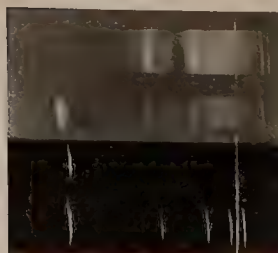


FIG. 2.

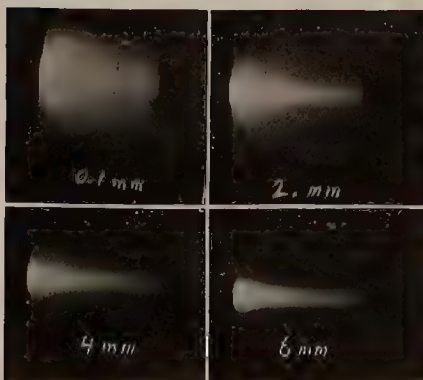


FIG. 4.

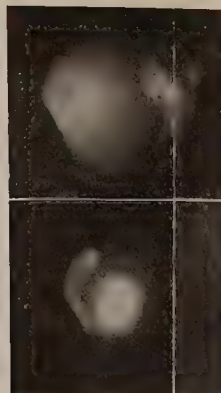


FIG. 5.

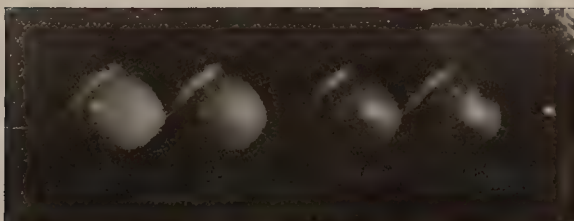


FIG. 6.

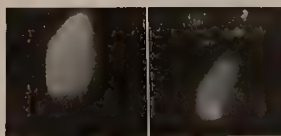


FIG. 7.



A

B



C

D



E

F

FIG. 7.

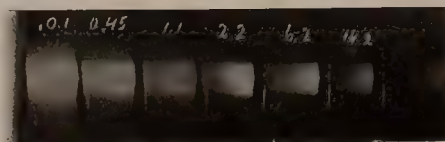


FIG. 12.

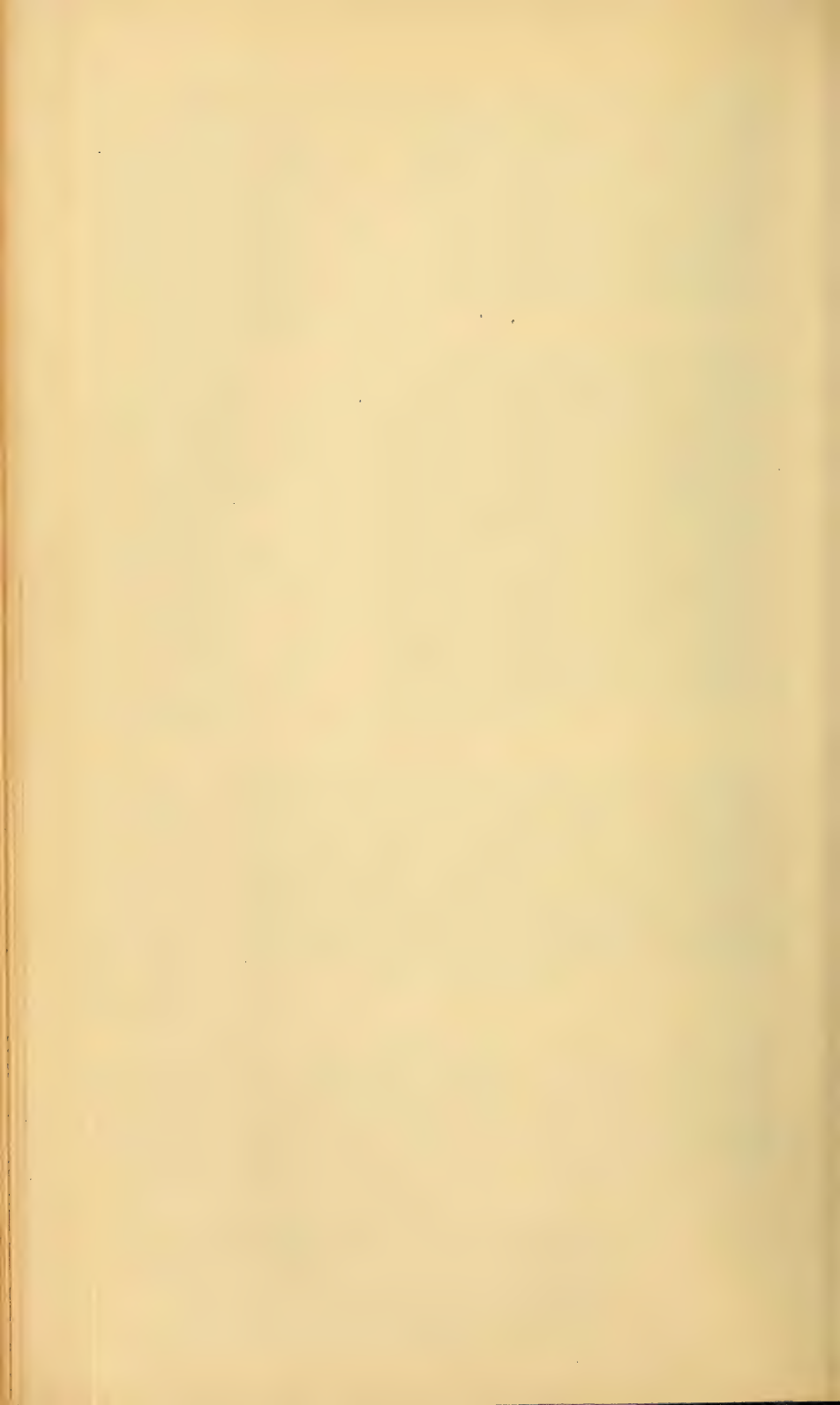




FIG. 8.



FIG. 9.

FIG. 11.

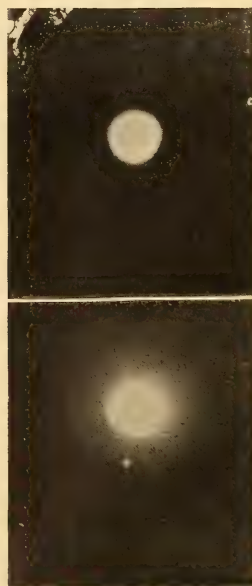
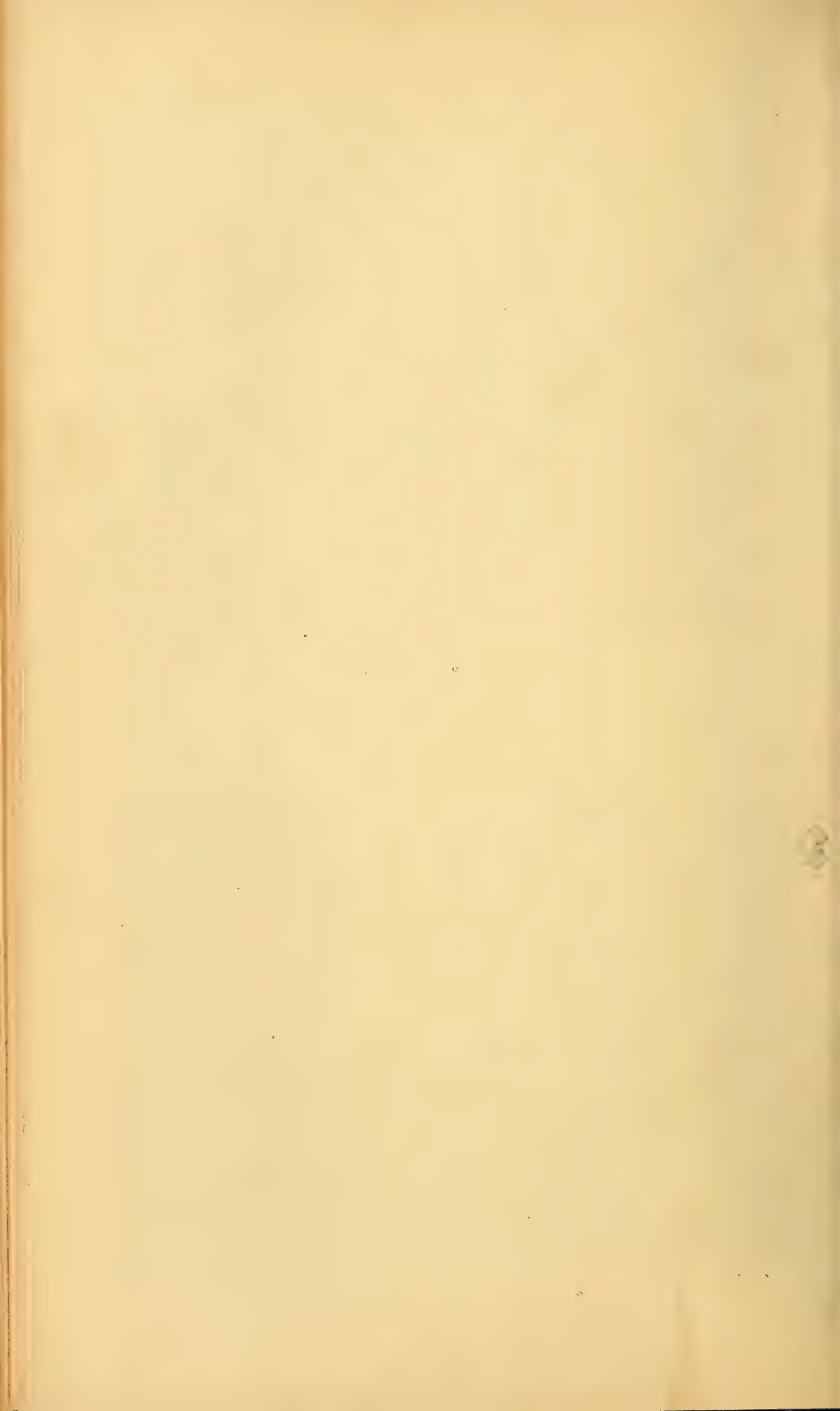


FIG. 10.



THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

JUNE 1912.

LXXXVII. *On the Nature and Velocity of Migration of the Carriers of Electricity in Flames containing Metallic Vapours.* By E. N. DA C. ANDRADE, B.Sc., Ph.D., 1851 Exhibition Scholar of University College, London*.

§ 1. *Introduction.*

THE experiments here described, which were carried out in the Radiologisches Institut of the University of Heidelberg, are primarily concerned with the velocity of migration and origin of the positive carriers of electricity which are formed when a metallic salt is brought into the Bunsen flame. Lenard† has shown that if a bead of a salt of one of the alkali metals be brought into the Bunsen flame, the coloured streak so formed is deviated in an electric field, and behaves as if positively charged. He estimates the velocity of migration of the carriers in unit field from the inclination of the luminous streak, and the upward velocity of the flame. Previously to Lenard's paper H. A. Wilson‡, using two horizontal electrodes in the flame itself, had measured the velocity of the positive carriers by driving them down against the current of the flame gases: he estimates the field required to bring them to the lower electrode by the current between the electrodes. The value obtained by Wilson is about 1000

* Communicated by Prof. Sir J. J. Thomson.

† P. Lenard, *Ann. der Physik* (4) ix. p. 642 (1902).

‡ H. A. Wilson, *Phil. Trans. A.* cxlii. p. 499 (1899).

times as great as that of Lenard, e. g. for lithium he finds $63 \frac{\text{cm.}}{\text{sec.}} \frac{\text{volt}}{\text{cm.}}$ and Lenard $0.08 \frac{\text{cm.}}{\text{sec.}} \frac{\text{volt}}{\text{cm.}}$. From this Lenard (*loc. cit.* p. 647) infers the probability of the existence of two kinds of positive carriers, but there appears to have been no attempt made to demonstrate this with certainty, or to explain the discrepancy.

It seemed to me desirable to establish clearly the simultaneous existence of, and distinguish the difference between, the two kinds of positive carriers, and especially to show the existence of both kinds with a common method. The arrangement adopted was similar to that used by Lenard for deflecting the coloured streak, the electrodes being vertical and outside the flame: the Wilson carriers, which are invisible, are then driven sideways out of the flame, and detected as described later. Their velocity has been measured, and found to be smaller than that given by Wilson; experimental and theoretical grounds are brought forward for supposing that Wilson and subsequent experimenters using his method have made an erroneous assumption as to the origin of these carriers, which makes the velocity work out too high.

It has been shown in the course of the work to be described that the faster positive carriers are metallic, like the slower ones, probably metal atoms, thus contradicting the theory that the positive carriers in flames are hydrogen. Experiments have also been made on the negative carriers, showing, among other things, that metallic negative carriers exist.

For convenience the slower positive carriers which form the luminous streak, whose velocity was measured by Lenard, will often in the following be called "carriers of the first kind"; the faster carriers, not seen as luminous, measured by Wilson, "carriers of the second kind."

A critique of previous work on the subject will be found at the end of the paper.

§ 2. *Method and Apparatus.*

The essence of the method is as follows: the flame is placed between two plate electrodes, one earthed, and the other insulated and connected with an electric machine; the fast moving positive carriers are in this way driven sideways out of the flame, and some of them fall upon an insulated platinum strip, which is connected to earth through a high resistance galvanometer, and is fixed close to the earthed

electrode, so that the uniformity of the field is not disturbed by it. The presence of the carriers is detected by the current through the galvanometer caused by the introduction of the bead of salt into the flame.

The earthed electrode is a massive brass plate, 6 cm. $\times$ 8 cm. $\times$ 0.5 cm.; to this is fastened a strip of brass pierced by a vertical slot, in which runs a brass piece holding an amber insulation: through the amber passes a stout wire holding the horizontal strip of platinum foil, 4 mm. $\times$ 50 mm., close to and parallel to the electrode. The brass piece can be clamped by a screw at any given height, and its position read off on a scale fastened to the slot. The other electrode is a brass plate similar to the earthed electrode, but insulated on amber; it is joined up to a "Mercedes" influence machine, through a reverser arranged so that either pole can be connected to the electrode, the other to earth. Between the electrodes, not touching either of them, burns a non-luminous flame of air and gas from a burner provided with a quartz flame piece, giving a flat flame about 20 mm. wide and 6 mm. thick, the plane of the flame being at right angles to that of the electrodes. By means of a small electromagnet, the current through which is controlled by a variable resistance, a platinum loop containing the given salt can be brought gradually into the flame; the platinum wire is insulated from the iron armature which supports it. The galvanometer, one pole of which is connected to the insulated platinum strip, the other to earth, is of the D'Arsonval type, with a resistance of 10,000 ohms; it is usually shunted with a resistance of 1900 ohms.

The potential of the insulated electrode is kept constant by a spark-gap connected in parallel. This potential is measured on a rough electrometer; the potential fall in the flame by means of two parallel "probes" of fine platinum wire placed in the flame itself, and connected to a small aluminium leaf electrometer, which is insulated, the outer case being connected to one probe and the leaf to the other. The electrometer is protected by an earthed net. For the smaller potential falls used in the final and more accurate experiments on the velocities of the faster carriers, a bifilar electrometer is used, the two threads being in this instrument surrounded by an insulated cylinder inside the outer metal case, which outer case is earthed.

The probes are placed in the flame between the luminous streak and the negative electrode; it then makes practically no difference in the potential fall whether the streak is present or not. If the potential difference is measured in the

luminous streak itself, it is found to be smaller than in the pure flame, but, with such amounts of salt as were used, by not more than 20 per cent. It is to be noticed that this is the case when the potential is maintained by cold electrodes *outside the flame*; when the electrodes maintaining the potential are platinum glowing in the flame, as in all previous experiments on the velocity of the faster positive carriers, the case is very different, the distribution of potential being very much altered by the presence of the salt in contact with one or both of the glowing electrodes.

§ 3. *Determination of the Velocity from the distribution of the faster carriers.*

When the insulated platinum strip is opposite the flame, and the insulated electrode is positively charged, there is a deflexion of the galvanometer, which remains constant as long as the field remains on: this is due to positive carriers present in the pure flame being driven out onto the strip. On the introduction of the bead of salt into the flame a further deflexion in the same direction is observed, showing that there are positive carriers which can be driven out of the flame contained in the metal vapour. The amount of this further deflexion gives a measure of the number of metallic carriers arriving at the particular region occupied by the strip. The extra current due to the introduction of the metal salt into the flame will in future be referred to as the "metallic current," and the corresponding deflexion of the galvanometer as the "metallic deflexion."

The fields used were usually not strong enough to produce a marked deflexion of the coloured streak: this could always be produced by increasing the field, but the smaller fields were used as being steadier. Some measurements of the velocity of the Lenard carriers deduced from the deflexion of

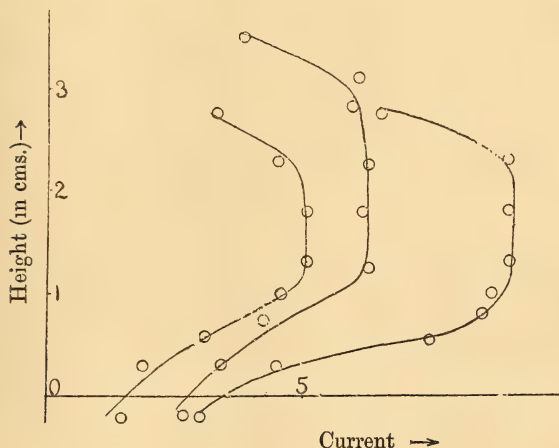
a just visible streak of vapour gave $0.04 \frac{\text{cm.}}{\text{sec.}} \sqrt{\frac{\text{volt}}{\text{cm.}}}$ for strontium*: Lenard gives $0.08 \frac{\text{cm.}}{\text{sec.}} \sqrt{\frac{\text{volt}}{\text{cm.}}}$ for lithium, and states that the velocity for strontium is smaller.

The distribution of the faster carriers was investigated by measuring the number of carriers, as measured by the metallic current, to be observed with the platinum strip at

* Since these measurements were made G. Ebert has published a paper (Heidelberg Dissertation, 1911) where he gives $0.042 \frac{\text{cm.}}{\text{sec.}} \sqrt{\frac{\text{volt}}{\text{cm.}}}$ for Sr.

different heights. When the strip was below or on a level with the bead of salt a small deflexion corresponding to positive carriers arriving on the strip was observed on the introduction of the bead, but for a certain portion above the bead this metallic current increased very rapidly with the height of the strip, and then remained approximately constant until the strip was in the neighbourhood of the top of the flame, when it again decreased. Typical distribution curves are shown in fig. 1. The ordinates are the vertical height of

Fig. 1.



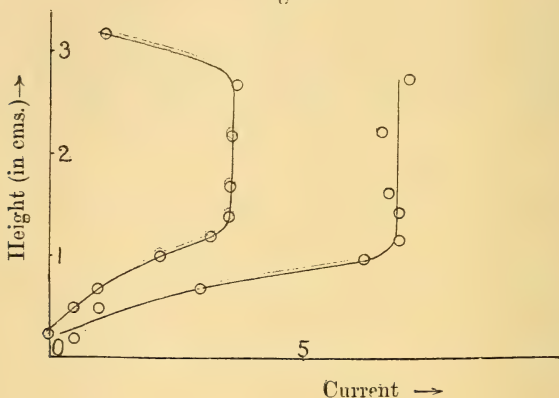
the mid line of the strip above the centre of the bead, the abscissæ the metallic deflexions *.

It seems reasonable to assume that the sudden increase of current is due to the strip being brought into the paths of the carriers coming from the lower part of the luminous vapour streak. The much smaller deflexions (which are, however, always present) for positions of the strip below this are then to be ascribed to positive carriers which have diffused down from the bead against the flame velocity. To test this point a screen, consisting of a very carefully insulated rectangle of thin platinum foil, was brought into the flame between the bead and the earthed electrode, so as to cut off the carriers below a certain point. The level of the top of the screen was well above the bead. The curves obtained are

* The three typical curves given were obtained on different days, when the height of the luminous streak was somewhat different. This accounts for the different extents of the flat maxima.

shown in fig. 2. The level of the top of the screen corresponds to the ordinate 0, and it will be observed that below this there is no current.

Fig. 2.



We make then the assumption that the height at which the flat maximum begins corresponds to the point at which the positive carriers from the lower part of the luminous streak (or from just above the screen, when the screen is used) arrive at the earthed electrode*. Then the velocity of migration of the carriers in the given field can be estimated from the vertical height of the strip above the screen for the position in which the large metallic current is first given. To do this we must, however, consider the effect produced by the portion of the path of the carriers lying in the hot air between the flame and the earthed electrode.

In the light of modern experiment it seems that positive carriers of molecular size do not become appreciably loaded with air molecules in such a case†. We have then to consider the effect of (1) the variation of the electric field, which is smaller in the flame than in the air-gap; (2) the variation of temperature; (3) the variation of the upward velocity of the gases.

* That there are present lesser currents between the point at which the maximum begins and the level of the top of the screen is due to the fact that the platinum strip is of finite breadth (4 mm.). The maximum first begins when the whole breadth of the strip is in the path of the carriers. By the height of the strip above the screen is therefore meant the height of the bottom of the strip above the top of the screen.

† See e. g. P. Lenard and C. Ramsauer, "Über die Wirkung sehr kurzwelliges ultraviolett Lichtes," *Berichte der Heidelberger Acad.* Part IV. (1911) page 19.

The variation of the velocity of a carrier of molecular size in a gas with the temperature can be deduced from a formula given by Lenard *

$$\omega = \frac{3}{2\pi\sqrt{2}} \frac{eF}{Ds^2W},$$

where e is charge, F the potential gradient, D the density of the gas, s the sum of the radii of carrier and gas molecule, and W the mean molecular velocity of the gas. Thus, assuming that the charge remains constant, we can find the ratio of the velocity in the hot air to that in the flame.

The upward velocity of the hot air will be less than that of the flame gases. The greater intensity of the field and the smaller upward velocity of the gases, together with the fact that the path in air is much shorter than that in the flame, tend to make the vertical rise of the carriers during their passage through the air-gap much smaller than that in the flame. Against this we have in the air a diminished horizontal velocity in unit electric field, owing to the lower temperature : this tends to increase the vertical rise in the air. Measurements were made to find the relative magnitudes of these effects. The strength of the field in the air-gap was estimated by measuring the field in the flame, and the potential difference between the electrodes ; the difference between the latter and the total fall in the flame gives the fall in the air-gaps. The temperature at different places in the air-gap was measured with a thermo-couple, and the upward velocity of the air at the same places compared with that of the flame by a method worked out by Becker †. It was found that, with the distances of our experiment, *i. e.* path in flame = 1.2 cm., path in hot air 0.8 cm., the vertical rise of a carrier in the air-path would be only $\frac{1}{15}$ of the total rise, on the above assumptions. This is chiefly due to the field being seven times as strong in the air, and the average upward velocity of the gases less than half that of the flame. (Later, we shall assume that the measured velocity is less than that given by the formula of Lenard's already quoted, because the positive carriers are not charged all the time, but are during a certain fraction of their journey neutralized by electrons present in the flame. Now there are far fewer electrons in the hot air than in the flame ; consequently the ratio of the horizontal velocity in the hot air to that in the flame will probably be greater than that assumed in the

* P. Lenard, *Ann. der Physik* [4] iii. p. 313 (1900). The original formula is more general.

† A. Becker, *Ann. der Physik*, [4] xxiv. p. 823 (1907)

calculation. Hence the vertical rise in the air will be still smaller.) The rise in the air can be neglected, as being not more than 7 per cent. of the total rise: our other measurements do not allow an assumption of greater accuracy. The whole vertical rise may, therefore, for purposes of calculation be assumed to take place in the flame.

For example, if we take the case for which the distribution curve is *a*, fig. 2, the whole vertical rise

$$= 0.95 \text{ cm.} = \frac{1}{\omega F} (360 + 26)$$

where ω = velocity of carrier in unit field in flame,

$$F = \text{strength of field in flame} = 150 \frac{\text{volt}}{\text{cm.}}$$

$$\left(\text{field in air} = 1100 \frac{\text{volt}}{\text{cm.}} \right),$$

and of the term in the bracket the first, 360, is proportional to the vertical rise in the flame, and the second, 26, to that in the hot air, which, as will be seen, is negligible.

$$\text{Hence } \omega = \frac{386}{150 \times 0.95} = 2.7 \frac{\text{cm.}}{\text{sec.}} \bigg/ \frac{\text{volt}}{\text{cm.}}.$$

The other curve in fig. 2 gives for ω $2.5 \frac{\text{cm.}}{\text{sec.}} \bigg/ \frac{\text{volt}}{\text{cm.}}$; while two careful experiments without the screen give 2.4 and $2.6 \frac{\text{cm.}}{\text{sec.}} \bigg/ \frac{\text{volt}}{\text{cm.}}$. Hence we may take the velocity of migration of the positive carriers of the second kind in the flame to be approximately $2.5 \frac{\text{cm.}}{\text{sec.}} \bigg/ \frac{\text{volt}}{\text{cm.}}$.

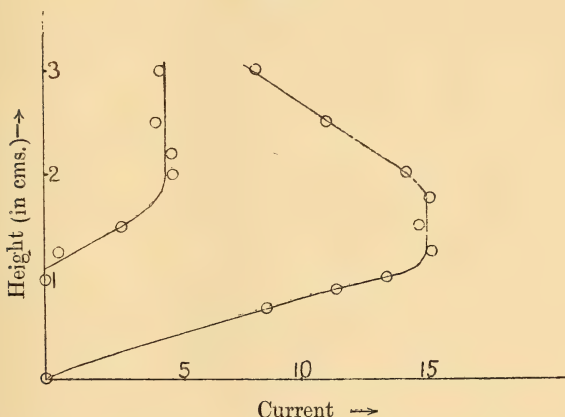
§ 4. Calculation of the Velocity without an Air-path.

An experiment made to see if the metallic current was markedly lessened by making the carriers pass through a greater distance in the flame (*i. e.* if many carriers were permanently neutralized) enables us to estimate roughly the velocity of the carriers without making any assumptions as to what takes place in the air-gap. The curves in fig. 3 show the resultant deflexions for the two cases:

- (1) in which the carriers pass through about 0.5 cm. in the flame;
- (2) in which the carriers pass through 1.4 cm. in the flame.

The bead was moved horizontally from one position to the other without altering the relative positions of the flame and the electrode. It will be observed that the metallic currents are very much less for all positions of the strip in the case when

Fig. 3.



the carriers pass through the extra centimetre in the flame, but further, that the maximum is reached at a lower position in the case where the path in the flame is short. If we assume that the vertical distance between the points at which the maxima begin in the two cases (0.65 cm.) is the vertical rise taking place in the 0.9 cm. of flame between the two positions, we can calculate the mobility. The potential gradient in the flame being $220 \frac{\text{volt}}{\text{cm.}}$,

$$\omega = \frac{0.9 \times 300}{230 \times 0.65} = 1.8 \frac{\text{cm.}}{\text{sec.}} \bigg/ \frac{\text{volt}}{\text{cm.}}$$

This is in as good agreement as we can expect with our previous values.

§ 5. *Action of Glowing Platinum on Metallic Vapours.*

It was also attempted to measure the velocity of the carriers without making them pass through air by bringing the earthed electrode into the flame itself. For this purpose the brass plate electrode was replaced by a very fine platinum net, fixed in the flame: an insulated platinum strip was so arranged that it could be moved in the flame vertically and close to the net. When, however, the net was earthed, and the strip connected to earth through a galvanometer, a

current, large compared with the usual metallic current, was obtained without any field being applied. The direction of this current corresponded to the assumption that negative charges were received by the strip, and was, no doubt, due to electrons shot out by the net (which from its fineness was much hotter than the strip) being received by the strip. If the net was insulated and earthed through the galvanometer, a current was observed if an earthed strip was present in the flame; if the strip was insulated or absent no current was obtained. In this case there must be approximate equilibrium between the accumulated electrons in the flame and those given out by the net, but as soon as an earthed strip is in the flame the electrons can escape as they are produced, and fresh ones are given out by the net, producing the observed current.

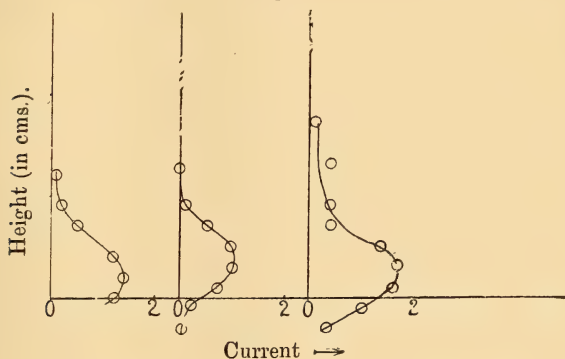
If the net is earthed, and the strip connected through the galvanometer to earth at a distance of about 1.5 cm. from it, the introduction of a bead of salt (SrCl_2) into the flame makes no appreciable difference to the observed current unless the luminous metallic vapour is in contact with the net, when the current observed from the strip is very much increased (four or five fold). If the strip in the flame is directly earthed, and the net earthed through the galvanometer, when the streak of luminous metallic vapour is brought into contact with the net, the current observed is increased in a similar manner. This shows that the impact of the metallic atoms of the vapour against the platinum must be able to liberate electrons in large quantities from the metals. The process may, of course, be considered not as direct impact, but as "Nähewirkung" (see P. Lenard, *Annalen der Physik*, [4] xvii. 1905, p. 244).

§ 6. *The Faster Carriers come only from the edge of the Luminous Vapour.*

To see if the fast moving positive carriers were driven out from throughout the volume of the metallic vapour, or only from the edge of the luminous streak remote from the positive electrode, as was suspected, a second bead of salt was brought into the flame between the first bead and the positive electrode, and level with the first bead. It was found, with the platinum strip in various positions, to produce no appreciable increase in the galvanometer deflexion. Hence it may be assumed that the faster carriers do not proceed from the volume of the vapour, but travel out from the neighbourhood of the edge only. This is most important for our theoretical considerations.

The insulated screen of thin platinum foil, pierced with a rectangular horizontal slit (3 mm. $\times$ 12 mm.), was brought into the flame between the bead and the earthed electrode, and arranged in different experiments with the slit at various heights above the bead. Curves of the type shown in fig. 4

Fig. 4.



were obtained in all cases ; the maxima are sharp considering the breadth of the slit. (These curves are taken at random as typical ; they are not all three made with the same bead.) This indicates that the carriers have all approximately the same velocity ; the fact that curves made at different heights with the same streak of vapour give all about the same maximum deflexion indicates again that the carriers proceed only from the edge of the luminous streak, for the streak increases in breadth as we go upwards. The very flat maxima in the curves obtained for the unscreened streak offer additional confirmation of this point. (See fig. 1.)

The effect of increasing the air-gap between the flame and the earthed electrode was examined. It was found to diminish markedly the metallic current for all positions of the platinum strip. An example of the effect is shown in fig. 6 ; the solid and dotted curves on the right of the figure represent respectively the metallic current obtained with an air-gap of 8 mm. and 18 mm. respectively. The same figure exhibits the effect for negative carriers to be referred to later. This shows that a certain number of the carriers become permanently neutralized, and pass upwards.

§ 7. *The Faster Carriers are Metallic.*

It was observed that if the platinum strip was carefully cleansed in the Bunsen flame before being used to detect the carriers, yet it afterwards gave the sodium colour in the

flame (if a bead of a sodium salt were employed), indicating that the faster carriers are metallic. Owing to the difficulty of avoiding small traces of sodium, the point was systematically investigated with strontium. With a bead of this metal in the flame, after a quarter of an hour in the field, a large metallic current being observed all the time, the strip showed the strontium lines very distinctly on testing in the Bunsen flame with a pocket spectroscope. Control experiments (1) with the bead in the flame, but no field, (2) with the field, but with the strip in a position in which no metallic current was observed (*i. e.* below the bead), (3) with the isolated plate charged negatively, gave no strontium. To put the matter to a rough quantitative test the galvanometer was calibrated, and the amount of strontium corresponding to a unit deflexion for a unit time calculated on the assumption that the strontium atom had two elementary positive charges, as in electrolysis. Solutions of SrCl_2 were made, one drop of which from a given pipette held a known quantity of strontium. Drops of the different solutions were brought successively upon a platinum strip similar to that used to receive the carriers, and slowly evaporated; the brightness and duration of the strontium lines produced on bringing this strip into the Bunsen flame were compared with the lines given by the electrically deposited strontium. The experiments showed that the amount of strontium deposited was, very roughly, that calculated: the experimental errors of this method are, of course, large, but it would probably detect a difference if one of the amounts were double the other.

Further experiments were then made on the transport of sodium. As a control, two platinum strips were arranged close to the earthed electrode, one being earthed through the galvanometer as usual, the other being connected with the insulated electrode, which was then maintained at a positive potential for some minutes. The earthed strip showed the sodium colour strongly in the flame, the other strip did not. The strips were interchanged, with the same result. Hence there seems no doubt that the transport of sodium is connected with the metallic current.

Measurements were made of the time in which, for a given galvanometer deflexion, enough sodium was transported to give a just perceptible coloration of the flame. Aselman* has given for the amount of sodium which will give a perceptible coloration for one second in the Bunsen flame in a dark room, 1.5×10^{-8} mg. NaCl, which is equivalent to

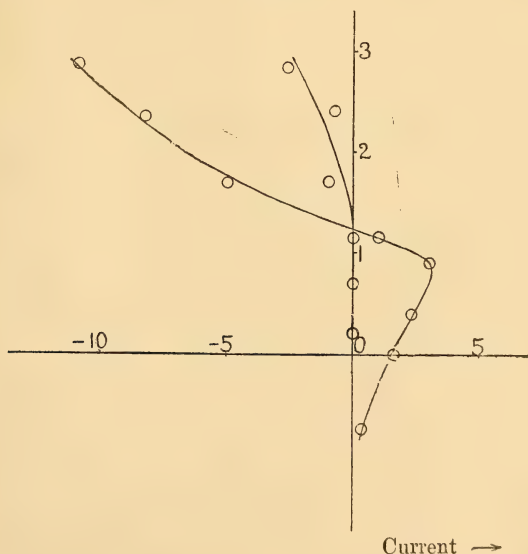
* E. Aselman, *Ann. der Physik* [4] xix. p. 960 (1906).

0.6×10^{-8} mg. Na. Our experiment was slightly modified to allow the tests being carried out under the same conditions as those of Aselman: on the assumption that each sodium atom conveyed one elementary charge, our observations of the current and time corresponding to the strip giving a just perceptible colour for one second on subsequent testing, gave 1.0×10^{-8} mg. Na as the amount, which is in moderate agreement, considering the nature of the experiment.

§ 8. *Experiments on the Negative Carriers.*

Measurements of the current produced by the introduction of a bead of salt into the flame for various positions of the platinum strip were also made with the same arrangement of apparatus, but with the insulated electrode charged negatively. In this case, if the strip be horizontally level with the bead, the introduction of the bead causes the current to diminish. As the strip is raised, a point is reached where the introduction of the bead causes no change in the current, and after this the metal vapour produces the usual increase of current found for the positive carriers. A typical curve is shown in fig. 5.

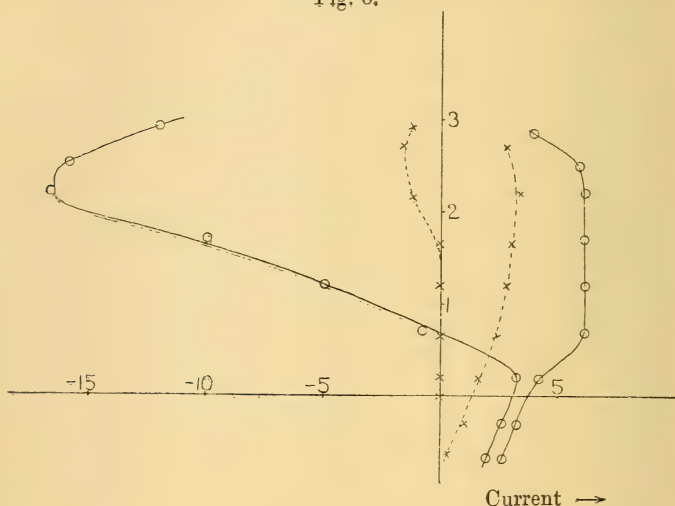
Fig. 5.



If the earthed electrode be further removed from the flame, the deflexions all decrease in the same way as with the positive carriers, but a path of 1 cm. extra in air decreases the maximum deflexion for the negative carriers to $\frac{1}{10}$, while

for the positive carriers it decreases it only to $\frac{1}{2}$. This is because the free electrons, which form the greater part of the negative carriers, become rapidly loaded with air molecules, and pass upwards with the current of air. For this, among many reasons, the velocity of the electrons cannot be estimated by this method. In fig. 6 are given curves for both positive

Fig. 6.



and negative, made for two different distances of the electrode and strip from the flame, the smaller distance being 0.8 cm., the greater 1.8 cm. Positive and negative readings were taken alternately by changing the sign of the electrode.

With Sr, as before mentioned, metal was not detected on the strip, when the electrode was negatively charged. With Na, however, the colour was unmistakably obtained with a run of a few minutes, though not nearly as bright as when the insulated electrode was positive for the same time.

The controls before enumerated rendered it certain that there really was a transport of metal on the negative side, though far less than on the positive side. This, together with the fact that about a thousand times as much Sr as Na is necessary to give a perceptible colour in the flame, would account for the Sr not being detected on the negative side. The presence of these metallic negative carriers enables us to explain the decrease of current which takes place on the negative side on introducing the bead if the strip is horizontally in the neighbourhood of the bead; this decrease is plainly shown in figs. 5 and 6. We assume that some of the

electrons of the flame get absorbed by neutral metallic atoms, which diminishes their velocity considerably: hence a certain number of electrons which before, in consequence of their high velocity, travelled almost horizontally out from the lower part of the streak of metallic vapour, now, combined with metal atoms and travelling slowly, arrive at the earthed electrode at a place higher than before: hence we get a diminished current for low positions of the platinum strip, but a considerable extra current above.

§ 9. *Theoretical.*

It has now been clearly established that when metallic vapour is present in a flame there exist positive carriers of two classes, distinguished by their having very different velocities of migration, the velocities of the one class being about $2.5 \frac{\text{cm.}}{\text{sec.}} / \frac{\text{volt}}{\text{cm.}}$ as compared with $0.04 \frac{\text{cm.}}{\text{sec.}} / \frac{\text{volt}}{\text{cm.}}$ for the other class in the case of strontium. Both kinds of carriers are metallic; the slower kind form a luminous streak. The faster kind produce no visible coloration in the flame when driven sideways out of the luminous streak; this is to be anticipated, since they are present in relatively very small numbers, as can be deduced from the time required to deposit a quantity of metal on the strip sufficient to produce strong coloration in the flame. The faster carriers are produced throughout the height of the streak, and hence their presence is not connected with the contact of glowing platinum, but inherent in the luminous vapour itself.

As a result of much experimental and theoretical work, Lenard has put forward with strong support the view that any single carrier of the class whose presence is detected by the visible deflexion of the luminous streak is not positively charged always, but only for a short fraction of the time*. We may now explain the difference of velocity of the two classes by supposing that in both cases the carrier is only charged for a fraction of the time, alternating the positive state with the neutral state, but that the fraction is very much greater for the one than for the other. We can calculate the theoretical velocity of a permanently charged carrier of atomic size from the formula given by Lenard already cited (p. 871), which has proved very successful †,

* *E. g.*, P. Lenard, *Ann. der Physik* [4] ix. 1902, p. 648, and [4] xvii. 1905, p. 238.

† For a short account of the formulæ for the mobility of carriers in a gas, see A. Becker, *Ann. der Physik* [4] xxxvi. p. 217 (1911).

Lenard gives as the mobility calculated from this formula the value $2.3 \frac{\text{cm.}}{\text{sec.}}$ in nitrogen at 2000°C.^* , but the diameter of the metal atom assumed by him is, according to work which has since appeared, too large, and the value of e too small. Taking for e the value 4.7×10^{-10} c.g.s. electrostatic units (Planck), and calculating the radius of the strontium atom from the value given by Becker $\dagger$ for the radius of the sodium atom, we have for the mobility of a permanently charged metallic atom $17 \frac{\text{cm.}}{\text{sec.}} \frac{\text{volt}}{\text{cm.}}$ (or for a molecule of SrO $15 \frac{\text{cm.}}{\text{sec.}} \frac{\text{volt}}{\text{cm.}}$). Thus we must assume, as we have

done above, that even the faster carriers cannot be always positively charged, but alternate the charged state with a neutral state caused by recombination with a free electron.

Evidence has been given for the assumption that the faster carriers come from a region near the edge of the luminous streak. Now in the streak itself we may assume that the impact of the metallic atoms against one another is the main cause of the liberation of an electron, and the consequent rendering of an atom positive; impact between a metal atom and a molecule of the flame-gases can also be sufficient to render an atom positive, but is a far less active cause $\ddagger$. In consequence of the large number of free electrons produced in the streak itself, the positive atom is quickly neutralized again; in fact from the velocity of the carriers in the streak the atom can, on the average, be positive for only about $\frac{1}{400}$ of the time. Now a metallic atom which is near the edge of the streak may, while it is positively charged, be driven out of or diffuse out of $\S$ the luminous streak, where the metal concentration is high, into the free flame remote from the positive electrode, where the number of free electrons must be small. Hence the average positive life of an atom which has arrived into the free flame near the earthed electrode will be much longer than that of an atom in the dense streak. From the calculated mobility of a permanently charged metallic atom, a carrier of the faster kind must be positive for about $\frac{1}{6}$ of the time.

* P. Lenard, *Ann. der Physik* [4] xvii. p. 197 (1905).

$\dagger$ A. Becker, "Über die Diffusion leuchtender Metalldämpfe etc.," *Sitzungsberichte der Heidelberger Acad.* 1911, p. 16.

$\ddagger$ E. N. da C. Andrade, "Some Experiments on the Electrical Behaviour of Metallic Vapours etc.," shortly to be published; and P. Lenard, "Über die Elektrizitätsleitung und Lichtemission etc.," *Sitzungsberichte der Heidelberger Acad.* 1911.

$\S$ Cf. p. 869.

It is interesting to compare the positive carriers in the flame with the canal rays in a vacuum-tube, which are also charged atoms. In both cases we have the constant alternation of the positive and neutral states *. Similarly, we have found in flames a result already known for canal rays, namely, that there exist metallic atoms in flames, in comparatively small numbers, which are negatively charged. These are analogous to the negatively charged atoms found in canal rays by Wien †, whose energy was much less than that of the positive ones.

In the following we give a critical resumé of previous work on the subject. H. A. Wilson, in the work already quoted (p. 865), obtained the value $60 \frac{\text{cm.}}{\text{sec.}} / \frac{\text{volt}}{\text{cm.}}$ as the

velocity of the positive metallic carrier, a value about 20 times as large as that found here for the carriers of the second kind. It is difficult, however, to determine exactly the smallest electric force which suffices to drive the carriers against the current of the flame-gases. Wilson measured the distribution of potential in the flame *without the presence of metallic salt*; he drew the potential curve and assumed that the smallest gradient here shown was sufficient to give the carriers the velocity of the flame. This smallest gradient lies, however, close by the positive upper electrode, in the place occupied by the metallic vapour in the experiment itself, and, since the carriers which come into account here proceed, as we think to have demonstrated, from the edge of the luminous vapour (*i. e.* in this case from the lower boundary of the vapour), and not from the upper electrode, this smallest gradient occurs in a region where the carriers are not necessarily driven down against the flame.

Moreau ‡ measured the velocity of the positive carriers with two vertical electrodes, one standing in metal vapour, the other in free flame, and assumed that the potential gradient was approximately uniform between the electrodes. This is far from being true (as Lusby has shown, for instance, in work to be quoted immediately); it is not to be wondered at that his value, $80 \frac{\text{cm.}}{\text{sec.}} / \frac{\text{volt}}{\text{cm.}}$, does not agree with mine.

* W. Wien, *Ann. der Physik* [4] xxvii. 1908, p. 1025. The result was first obtained by Lenard for flames (*Ann. der Physik* [4] ix. 1902, p. 649) and found again for canal rays by Wien, *cf.* W. Wien, *Ann. der Physik* [4] xxx. p. 368 (1909).

† W. Wien, *Ann. der Physik* [4] xxxiii. p. 871 (1910).

‡ G. Moreau, *Ann. de Chimie et de Physique* [7] xxx. p. 39 (1903).

E. Marx* has also measured the velocity of the positive carriers; he assumes, however, for the purpose of simplifying his calculations, that the whole ionization takes place in the body of the vapour, which is certainly incorrect when electrodes of glowing platinum stand in the metallic vapour, as in his experiments (*cf.* p. 874). His work is of great interest, but it is not adapted to give a correct value of the velocity.

When this work was practically completed a paper by Lusby† on the subject came to my notice, and a second paper by this author, including his previous results, has just been published‡. He brings forward criticism essentially agreeing with that already given here against the previous work. He has made measurements with Wilson's original method, but has measured the gradient of potential in the flame from one electrode to the other, with the salt vapour present in the flame. At normal flame temperature the gradient in the vapour is very small, that in the free flame large: Lusby takes the gradient in the vapour as the one relevant, which seems to be erroneous as already

explained. With this he gets a value of $290 \frac{\text{cm.}}{\text{sec.}}$ As he

has given the curve of potential for one case in his paper §, we can obtain the correct velocity according to the views here advanced. Taking the gradient in the flame just be-

neath the salt ($50 \frac{\text{volt}}{\text{cm.}}$), we get as the value of the velocity

$4.1 \frac{\text{cm.}}{\text{sec.}}$, which agrees pretty well with our average value

of $2.5 \frac{\text{cm.}}{\text{sec.}}$

His assumptions as to the gradient in question will account for a peculiar effect noticed by Lusby. He has made measurements at different temperatures, and finds that down to 1450° absolute the velocity is roughly proportional to $\sqrt{\theta}$, but that below this the values of the velocity are very much smaller than those given by $\sqrt{\theta}$. Now down to 1450° abs. the distribution of potential varies very little with the temperature, but below this the gradient in the vapour increases very much, and this is the main cause why

* E. Marx, *Ann. der Physik* [4] ii. p. 768 (1900).

† S. G. Lusby, *Proc. Cambridge Phil. Soc.* vol. xvi. part 1, p. 26 (1911).

‡ S. G. Lusby, *Phil. Mag.* Nov. 1911, p. 775.

§ *Proceedings Cambridge Phil. Soc. loc. cit.* p. 30.

the values given by Lusby are so much smaller than are given by $\sqrt{\theta}$. But in the pure flame the gradient decreases, though not very much, so that taking the gradient just below the salt vapour, the velocity per $\frac{\text{volt}}{\text{cm.}}$ would be relatively much larger than that given. Lusby does not give sufficient data to enable me to calculate the velocity according to the views here put forward*, but it looks possible that the $\sqrt{\theta}$ law holds roughly throughout the range.

To explain the large values obtained for the mobility, Lusby assumes that the positive carrier is always an atom of hydrogen. This is quite untenable, as it has been shown here experimentally that the carriers are metallic (§ 7). Particular attention is called to the fact that this was established for two metals (Sr and Na) and to the rough quantitative tests. Of course, none of this criticism of Lusby's paper affects his results, that the velocity is the same for all metals, except at very low temperatures: this result agrees with Lenard's formula for the mobility of a carrier of atomic size (see p. 871). His criticism of Lenard's early results on the deviation of the coloured streak in the electric field, based on the fact that chloroform removes the colour from the streak without much altering the conductivity (Smithells, Dawson, and Wilson) does not seem to me relevant. When glowing electrodes are in the vapour the liberation of an electron from the atom takes place mainly at the electrodes, and it is probable that while chlorine prevents the impact of metal atom against metal atom in the vapour liberating an electron, it does not stop this effect at the electrodes, and thus, while prohibiting "ionization" in the body of the vapour, does not much affect the conductivity†.

A short time ago H. A. Wilson‡ published a paper containing a theoretical treatment of the carriers in flames containing metallic vapours. He makes Lenard's assumption, also made here, that the carrier is only positive during a fraction, f , of the time. Through the further assumption that the velocity of the carrier is inversely proportional to the square root of the atomic weight, he obtains values of f , and he further obtains similar values from the conductivity relations of the salts. The values agree so badly, that it is hard to believe that they furnish a proof of the correctness of the hypothesis. Wilson comes to the conclusion that the

* The potential curves are all reduced to 100 volts scale.

† See Lenard, "Über die Elektrizitätsleitung und Lichtemission metallhaltiger Flammen," *Sitzungsberichte der Heidelberger Acad.* 1911.

‡ H. A. Wilson, *Phil. Mag.* June 1911, p. 711.

positive carriers are metal atoms, as my experiments have shown, so far as their accuracy allows. But as the observations of the brightness of the Sr lines produced by the Sr deposited on the platinum strip cannot be carried out very exactly, we can only assert with certainty, that the carriers cannot possibly consist of more than two atoms. We have very good grounds for assuming that the light emission is effected by single atoms, on which assumption Lenard has based his researches on the subject *. The results of experiments on the diffusion of sodium vapour in the flame also indicate this †. It is, however, not absolutely certain that the faster carriers are centres of light emission: they are present in such relatively small numbers that they could not be expected to be visible.

§ 10. *Conclusions.*

(1) The positive carrier in a flame containing metal vapours is of metallic nature, very probably the metal atom.

(2) The positive carrier has two different definite velocities of migration in the electric field, according as it is present in the streak of metallic vapour or in the free flame: in both cases it alternates the positive with the neutral state. In the former case it is charged for about $\frac{1}{4.00}$ of the time, in the latter for $\frac{1}{6}$ of the time.

(3) For strontium the greater velocity of migration is $2.5 \frac{\text{cm.}}{\text{sec.}} / \frac{\text{volt}}{\text{cm.}}$. There seems no reason to doubt the results of other experimenters, that the velocity is the same for different metals, which agrees with our theory. Hence this value probably gives the velocity of migration of an atom of any metal in the free flame.

(4) The presence of glowing platinum in the vapour causes the liberation of electrons from it in large quantities.

(5) There exist, besides the free electrons, negative carriers of the second kind which are metallic, in relatively small numbers. This gives an analogy with the canal rays.

This work was carried out in the Radiologisches Institut of the University of Heidelberg, to the Director of which, Professor P. Lenard, I am indebted for much help and encouragement. I also wish to express my thanks to Dr. Ramsauer for assistance and many valuable suggestions.

* P. Lenard, *Ann. der Physik* [4] xvii. p. 198 (1905).

† A. Becker, "Über die Diffusion leuchtender Metaldämpfe," *Heidelberger Acad.* 1911.

LXXXVIII. *Simultaneous Vibration Curves for Strings and Air of Violin.* By EDWIN H. BARTON, D.Sc., F.R.S.E., Professor of Experimental Physics, and WALTER B. KILBY, B.Sc., Research Scholar, University College, Nottingham*.

[Plates XIII.-XV.]

CONTINUING the work of one of us and others[†], the present paper treats of the simultaneous motions of the strings of a violin and the air at a sound-hole. In order to detect the vibrations of the air, part of this sound-hole was covered with a thin membrane connected to a rocking mirror.

Each string is dealt with separately and its vibrations simultaneously with those of the air recorded photographically. Further, the strings were each excited at two or more places by bowing, plucking, and striking.

A special feature of the present work is the series of photographs showing the *initial* stages of the motions. Some of these figures record not only the musical vibrations of the pitch of the string, but also the recoil and vibration of the violin as a whole, just after the string was plucked or otherwise excited.

EXPERIMENTAL ARRANGEMENTS.

A general plan of the optical arrangements is given in Pl. XIII. fig. 1. The light proceeds from the Leitz Lilliput Arc lamp A through the condenser C, in a nearly parallel beam. Part of this beam falls upon a screen with a pinhole H and proceeds thence to the small rocking mirror *m* (by Hilger). This mirror is concave and converges the light to the lower part of the photographic plate P. The other part of the beam from the condenser is caught by the plane mirror M₁, and sent to M₂ which reflects it to the slit S. A real image of this vertical slit is then focussed upon the string by the lens L₁. The light is then reflected by the plane mirror N, and a second real image is focussed by the lens L₂ on the upper part of the plate P. This plate is placed in the horizontal rails RR in a dark room, and in taking a photograph is shot along them by means of the indiarubber cords shown.

Thus the vertical vibrations of string and air combine with the uniform horizontal motion of the plate to give two

* Communicated by the Authors.

† Phil. Mag. July 1905, pp. 149-157; Dec. 1906, pp. 576-578; April 1907, pp. 446-452; Aug. 1909, pp. 233-240; Sept. 1910, pp. 456-464.

simultaneous displacement-time records of the vibration. The string's motion appears in the positive print black on a light ground and the air's motion white on a dark ground.

The place selected as most suitable to give the motion of the air was the lower circular part of the right-hand sound-hole (*d*, fig. 2). On this accordingly the very thin membrane was placed. But in a preliminary trial it failed to give sufficient motion when the other portion of the hole was left open. The other part was therefore closed by a covering of stiff white paper stuck on (see *pp*, fig. 2). This sufficiently intensified the motion at the lower end to make it recordable by the membrane and connected mirror. The connector consisted of a strip of aluminium foil of slightly curved cross-section to give stiffness. Its ends were attached to the membrane and mirror by little pieces of animal membrane and shellac. See Pl. XIII. fig. 3, in which *d* and *d'* show the normal and displaced positions of the membrane, *s* the connecting stalk, and *n* and *n'* the normals to the mirror *m* at rest and displaced. The mirror carried a fixed axle consisting of a needle fastened on behind it with a strip of aluminium and shellac. This axle rested in two V-pieces of aluminium and was held down by india-rubber bands.

Clamp Mounting.—In the first series of experiments, these axle supports were carried on an adjustable bracket clamped on to an outer corner of the violin, as shown in figs. 3 and 4, pl. vii., of a previous paper (Phil. Mag. Sept. 1910). This *clamp* mounting applies to figs. 1–22 of Pl. XIV. of the present paper. But it was felt that this mounting would detect any slight motion of the belly that occurred as well as that of the membrane relative to the belly.

Belly Mounting.—In order to obtain separate information as to the motions of the membrane relative to the belly in its immediate vicinity, a second mode of mounting was accordingly adopted. This is shown by figs. 2 and 4, from which it may be seen that tiny aluminium brackets support the axle and rest on little packing-blocks of wood on the belly, the whole being fastened by shellac.

This *belly* mounting was used in obtaining figs. 23–33 of Pl. XIV. and for all the figs. 34–61 of Pl. XV.

Initial Motions.—Usually the plates were shot in the rails by one operator after he had heard the sound properly elicited by the other. The plate thus passed rapidly by the opening in the partition very shortly after the commencement of the sound and so showed the character of the motions when just *established*. The elastic threads were

arranged to have no tension (and so produced no acceleration) when the plate passed the opening and secured the exposure.

This method left little or nothing to be desired when the strings were bowed, as that excitation sustained the motions till the photograph was taken. Moreover, with a bowed note the sustained motion is of chief interest.

But this method did not succeed so well for transitory effects. Thus, in attempting to photograph the vibrations excited by plucking or striking the records obtained were repeatedly disappointing. The string's motion was often of considerable amplitude, while the spot of light from the mirror connected to the membrane scarcely stirred. This was the more surprising since on observing the spot on a screen in place of the plate, it appeared to have a transitory motion of distinctly appreciable amplitude. It therefore seemed as though after plucking the string the vibrations of the air were at first large, but died away before the plate could catch them by the ordinary method of shooting.

After trying several ways designed to record this large initial vibration (or displacement), the following method seemed best and was adopted. The plate was placed in the rails but kept in the dark till about a second before the string was plucked or otherwise excited. When this preliminary signal was given the plate was slid into the exposure position by hand and there held against the tensions of the elastic cords. Immediately the string was excited the plate was released. The *very tight* elastic cords attached to it (for this method of shooting) then gave it the besired acceleration and revealed the special *initial* features of the motions.

But since on this plan a pause occurred with the plate in position and exposed to stray light, it was necessary to use the pierced black diaphragms D_1, D_2, D_3 , fig. 1, Pl. XIII., and black velvet screens V, V, V, V, V, V, to prevent the fogging of the plate.

Magnifications.—The string was usually illuminated by the real image of the slit at 5 cm. to 12 cm. from the nut (*i. e.*, end of the string remote from the bridge). On the original negatives and prints the magnification of the motion of this part of the string is obviously $L_2P \div NL_2$. These values were 139 and 36 cm. respectively and give a quotient of 3.86 nearly.

The magnification of the membrane's motion is double the quotient: mP divided by the arm of the attachment of stalk to mirror. Now mP , the distance from mirror to plate, was 160 cm., and the small arm on which the stalk acted

was of the order 0.12 cm. Hence the magnification of the membrane's motion on the negatives was 2667 nearly.

Thus the ratio of magnifications of motions of membrane and string on the originals, or any reproductions of them, is of the order $2667 \div 3.86 = 691$ nearly. Or, in other words, the membrane's motion is magnified nearly 700 times that of the string's motion.

RESULTS.

One hundred and forty plates were exposed, and of these sixty-one reproductions are here presented.

These naturally fall into three series, those taken under the ordinary conditions of shooting, *first*, with the clamp-mounting of the mirror; *second*, with the belly mounting; *third*, those taken under the special conditions of shooting to record the initial stages of the motions, the belly mounting being here retained.

The distances from the bridge at which the strings were excited are stated near each figure as a fraction of the string's length. In these marginal references "plucked" means plucked by the finger-tip; "plucked by plectrum" refers to excitation by the point of a pencil. "Struck" denotes a blow struck by a lead-pencil padded with two or three thickness of wash-leather; "struck by wood," refers to a blow by the naked edge of a hexagonal pencil.

As to the interpretation of the abscissæ and ordinates of the curves on the prints:—

(1) The beginning of the time is in all cases at the left-hand side.

(2) The ordinates for the strings' motions are always inverted.

(3) The ordinates for the membrane's motion are also inverted.

Clamp Mounting.—The first series of figs. 1-22 of Pl. XIV. deals with the motions obtained when the mirror axle was supported by a bracket clamped at a corner of the violin.

Fig. 1 for the G-string bowed at $\frac{1}{4}$ shows a good two-step zigzag for the string as it should do, and also a large and characteristic motion for the air. This motion is much feebler and less marked in the next figure for the same string bowed at $\frac{1}{5}$. Fig. 3 shows a large motion of the plucked string, but only a moderate motion for the air by this method of shooting. The air's motion recorded in

fig. 4 by plucking is still less and in fig. 5 by striking is scarcely perceptible.

We now pass to the D-string for which figs. 6 and 7 record the air's motion when the string was bowed. It is here noticeable that the string does not appear to move. This is because the bowing must be about horizontal on the D-string to clear the G- and A-strings on each side of it. The motion of the D-string elicited by bowing is accordingly nearly horizontal and so escapes detection on the plate. The air's motion in both figures shows that the string was really vibrating. Figs. 8 and 9, again, show the motion of the string, because it is now plucked and therefore vibrates vertically. But in spite of the large amplitude of the string's motion, that of the air is small. Figs. 10 and 11 dealing with the D-string plucked by plectrum yield a similar comparative amplitude of the spot. Figs. 12 and 13 for the D-string struck give still smaller comparative amplitudes of the air's motion.

Figs. 14 for the A-string bowed at $\frac{1}{4}$ exhibits an air motion with considerable similarity to figs. 1 and 6 for the G- and D-strings bowed at $\frac{1}{4}$. Fig. 15, for the A-string plucked, is given as a specimen of the many disappointments encountered in the work. For it shows no appreciable amplitude in the air's motion, although the string was going so well. It was the frequent recurrence of this kind of result which urged us to adopt the special method of shooting for plucked strings as given on the other folding plate. Figs. 16-22 dealing with the E-string show a marked resemblance throughout, but a dissimilarity from the other strings. This may be due to the close proximity of this string to the sound-hole under examination. It is noteworthy that large comparative amplitudes of the spot are obtained throughout, but very strange that the various excitations give almost identical curves. The tones elicited were good throughout.

Belly Mounting.—The second series of figures, 23-33 deals with the motions recorded when the mirror was mounted direct on the belly as shown in figs. 2 and 4, Pl. XIII. The motions for the G-string are represented by figs. 23-28, which show very little vibration of the air for plucking (figs. 27-28), but by bowing show a very fair motion (figs. 23-26). These should be compared with fig. 1, showing the result obtained with the clamp mounting.

For the D-string only one record, fig. 29, seemed worth presenting, the others giving inappreciable amplitudes of the

spot. This is an example of what holds throughout the work, that where few records are presented for any string, the others were of very small amplitude. For each string the effects of ten or more excitations were examined and often plates exposed for all.

Fig. 30, showing the effect of bowing the A-string, gives a very curious curve for the air's motion. This is partly due to the failure of the spot in this case to move quite vertically.

The remaining three figures, 31-33, deal with the E-string bowed, the various other modes of excitation showing very little motion by the ordinary method of shooting then in use. As, in this string, bowing at $\frac{1}{7}$ and at $\frac{1}{4}$ gave very small motions of the spot, bowing at $\frac{1}{20}$ was tried. But this (fig. 31) gave such a violent motion of the mirror, that the spot failed to move strictly in a vertical line. This accounts for the curve on the record being slightly undercut.

Comparison of Records for Clamp and Belly Mounting.—Glancing broadly over the two series, figs. 1-22 and 23-33, we see that the former gives *simpler* curves of *larger* amplitudes than the latter. Passing to a detailed comparison we may notice that some excitations of particular strings shown in the first set are not represented in the second, although the attempt to obtain these was made.

As to the interpretation of each set, we may note that the second smaller series (figs. 23-33) obtained with the belly mounting probably gives more strictly the pulsations of the air in the sound-hole relative to the surrounding part of the belly.

But the figures of the former set (figs. 1-22) obtained with the mirror mounted on the bracket clamped at the corner are of interest as perhaps giving more nearly the effects heard. For, since the corner of the violin in question is very inert, the motion of the membrane with respect to it probably represents the vibrations of the air originated by that part of the violin and thence reaching the hearer.

Initial Motions.—The photographs taken under the special conditions of shooting to record the initial motions are given in figs. 34-61 of Pl. XV. Of these, ten (34-43) deal with the G-string, four with the D-string, and of the remaining figures seven each deal with the A-string and E-string.

Owing to the plate being held in position ready for the excitation of the string, strong lights are shown on the prints just where the holes occurred in the diaphragm.

Further, it is seen in each figure that after the plate was released the velocity was accelerated, and accordingly the wave-length of the record increases from left to right.

In the case of bowing and some of the other excitations of the string it will be seen that the spot suffers no large sudden displacement at the commencement of the vibrations (see figs. 34, 35, 38, 40, 42, 46, 53, 59).

But often with plucking there is a sudden shift of the spot at the instant of the excitation (see figs. 37, 44, 45, 49, 50, 51, 55). This shift is probably due to the yield of the violin, as a whole, under the deflecting action of the finger holding the string up before the release. On the release, the violin, regarded as a deflected beam, then springs back. Further, the violin sometimes vibrated as a whole after the shock of this release or under a blow struck. For a comparatively long wave of these slow vibrations is shown on figs. 37, 41, 43, 44, 50, 51, 52, 60, 61.

Fig. 58 shows first a slow vibration rapidly damped out, succeeded by a longer wave vibration on which are superposed the motions corresponding to the musical vibrations proper to the E-string.

As to the duration of the slow vibration of the spot shown as a long upward half-wave near the centre in figs. 44, 50, and 51, the time is found to be of the order of one-fortieth of a second, corresponding to a frequency of twenty per second. This time is estimated by counting the corresponding vibrations of the string shown on the upper part of the plate. The strings were always tuned to concert pitch and so had approximately the following frequencies :— G, 203·4 ; D, 305·1 ; A, 457·7 ; E, 686·5.

All the figures 34–61, taken by this special method of shooting, explain why it was impossible to obtain by the other method any large amplitude of the spot's motion by plucking or striking. For, as now shown, the spot's amplitude in the musical vibration corresponding to the pitch of the string is always small, with this belly mounting of the mirror. The large motion of the spot (often observed to occur on a fixed screen put in place of the plate) is now seen to be due simply to the sudden shift of the violin as a deflected beam on the release when plucking or on receiving the blow when striking.

University College, Nottingham,
January 26th, 1912.

LXXXIX. *A Kinematic Method of finding the Roots which are less than Unity of a Rational Integral Equation of any Degree : followed by a more general Method of finding the Roots of any Value.* By THOMAS H. BLAKESLEY*.

I. *A kinematic method of solving a rational integral equation of any degree for roots less than unity.*

THE method depends mainly upon two facts, one of a mathematical character, the other kinematical.

The mathematical proposition is that every integral power of $\cos \theta$, as $\cos^n \theta$, may be expressed in a finite series of terms involving one only of the quantities $\cos n\theta$, $\cos n-2\theta$, $\cos n-4\theta$, &c., the last term involving $\cos \theta$ if n is odd, and not involving θ , or absolute, if n is even.

The kinematical fact is that with an appropriate system of links it is possible to make a series of points move so that the polygon formed by joining them will always remain equiangular, though the angle between its consecutive sides will vary, the sides themselves being at the same time maintained in any given ratio among themselves, though not to a fixed unit†.

Suppose a given equation to be

$$0 = A + Bx + Cx^2 + \dots + Nx^n,$$

and substitute $\cos \theta$ for x , then

$$0 = A + B \cos \theta + C \cos^2 \theta + \dots + N \cos^n \theta.$$

If now for every power of $\cos \theta$ is substituted its value in cosines of multiples of θ there will result an equation of the form

$$0 = R_0 + R_1 \cos \theta + R_2 \cos 2\theta + \dots + R_n \cos n\theta,$$

in which the coefficients $R_0 \dots R_n$ are readily obtained linear functions of the coefficients $A B \dots N$, of the original equation.

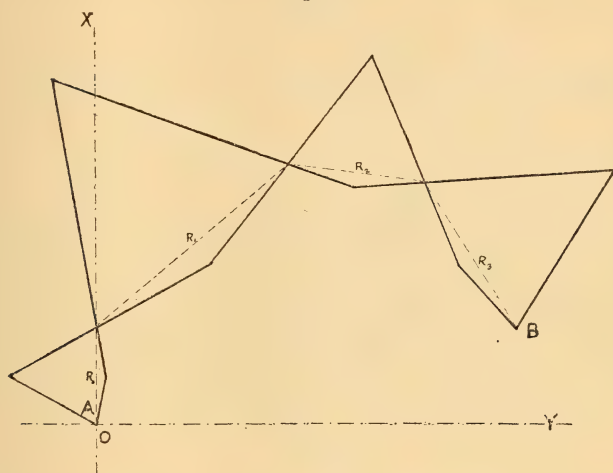
Now suppose an equiangular polygon formed (fig. 1), with the sides proportional to $R_0 \dots R_n$ taken in order and laid end to end. Upon each side erect an isosceles triangle with sides proportional to the chord which forms its base, and in every case extend the sides beyond the base until the nearer sides of the next-but-one triangles intersect, finishing the first and last cases in an obvious way.

* Communicated by the Author.

† For an introduction to the ideas involved in this sort of motion, *vide* a paper on "Logarithmic Lazytongs and Lattice-works," in the Philosophical Magazine of September 1907.

This will result in a number of kite-shaped figures whose diagonals joining equal angles are in the ratio $R_0 \dots R_n$.

Fig. 1.



Now suppose bars to take the place of the lines drawn, not ending, however, where the kites join, but continuous across such points from the tail-end of one kite to the head of the next; joints are supposed at all points where such bars either join or cut one another, of the nature of pins round which the bars can turn.

Such a system is a linkage capable of a proper motion which will always maintain the chords $R_0 \dots R_n$ in the same ratio among themselves, as well as equiangularity in the whole polygonal train, though the angle between any two consecutive chords will vary.

Let A and B be the extremities of the linkage. Take a pair of rectangular axes Ox , Oy , and suppose A to be pinned down at O , and make the other extremity of R_0 lie in Ox , and let θ be the angle between any two consecutive sides of the polygon externally.

Then clearly the projection of AB upon line Ox is proportional to

$$R_0 + R_1 \cos \theta + R_2 \cos 2\theta + \dots + R_n \cos n\theta.$$

But the equation requires that this shall be zero.

If, therefore, the proper motion is given to the linkage, always keeping R_0 in Ox , until the point B is found in Oy , in that position R_1 makes with Ox the angle θ whose cosine

is a root of the equation, or the projection of R_1 upon Ox divided by R_1 is a root.

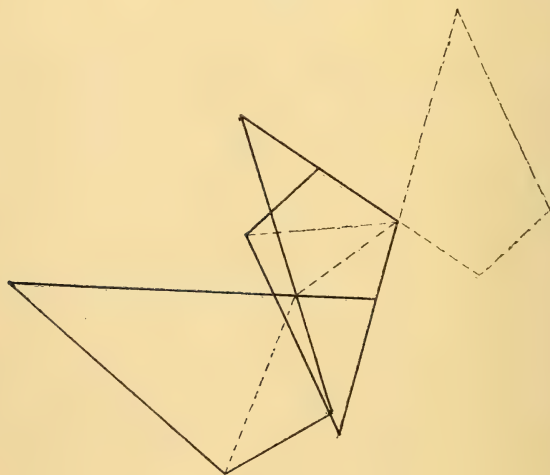
It may be pointed out that the projection of AB upon Oy in any position of the linkage is

$$R_1 \sin \theta + R_2 \sin 2\theta + \dots + R_n \sin n\theta.$$

This plan is obviously applicable only to roots which are less than unity numerically. The roots which exceed unity might be found by writing $x = \frac{1}{y}$ in the original equation, and solving the resulting equation for y in a similar manner.

Should the coefficient of a term in the cosine form of the equation be negative, the corresponding kite must be turned in its plane through 180° from the position it would have occupied had the coefficient been positive, round the point of junction with the preceding kite. The sides adjacent in the two kites concerned will still be continuous, and the bars incorporated as before, as shown in fig. 2, where the dotted

Fig. 2.

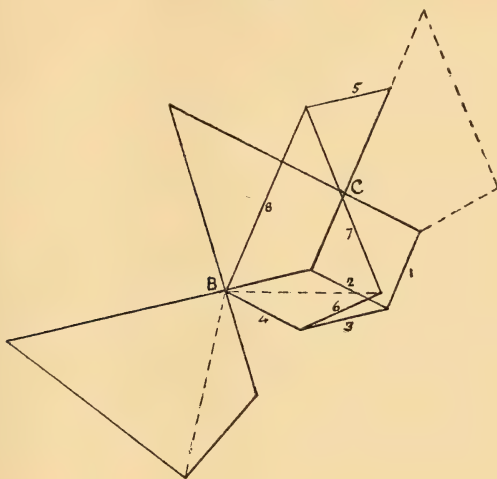


outline represents the position the second of the two kites would have occupied if the coefficient had been a positive one. It may here be noticed in regard to the position of all the kites, positive or negative in their chords, that if an observer traverses the series of chords in order from end to end, he will always have the similar ends of all kites on the same side of him.

An important point arises if one of the coefficients in the

cosine form of the equation vanishes. Suppose, for instance, that R_1 R_3 have finite values but that $R_2=0$. The difficulty may be surmounted in the following way (fig. 3).

Fig. 3.



A kite in the angular position of that corresponding to R_2 is inserted for the purpose of ruling the angular motion of R_3 . It may be of any finite size, and therefore equal in all respects to the kite upon R_3 . It is then necessary to translate as it were the third kite until its first point coincides with the second of the first kite. This can be virtually done by supplying the remainder of the links shown.

Nos. 1, 2, 3, 4, 5, and 6 are each one equal to the shorter side of the third kite, Nos. 7 and 8 to its longer side. No. 5 is parallel to No. 3, and attached to the longer side of the third kite so as to secure this, *i. e.* its point of attachment will be at a distance from the tail of the third kite equal to one of its shorter sides. Should the third kite have R_3 negative the case presents no particular difficulty. In these cases some of the sides of the linkage can be dispensed with. In fig. 3 the final two sides of the third kite may be omitted.

II. *The kinematic determination of the roots of an equation, of any magnitude.*

Suppose the equation to be

$$0 = \{ A + Cx^2 + Ex^4 + \dots \} \pm N x^n.$$

The last term will appear as $+Nx^n$ in the first bracket if n is even, in the second if n is odd.

Let

$$x = \tan \theta = \frac{\sin \theta}{\cos \theta},$$

and substitute for x this value. Then

$$0 = \left\{ A + C \frac{\sin^2 \theta}{\cos^2 \theta} + E \frac{\sin^4 \theta}{\cos^4 \theta} \dots \dots \dots \right\} \\ - \left\{ B \frac{\sin \theta}{\cos \theta} + D \frac{\sin^3 \theta}{\cos^3 \theta} + F \frac{\sin^5 \theta}{\cos^5 \theta} \dots \dots \right\}.$$

Reducing each line to a common denominator, which will be some power of $\cos \theta$, and cancelling out as far as possible, it is to be noticed that if n is even there will remain $\cos \theta$ in the denominator of the first line; if n is odd, in that of the second. Multiplying through by $\cos \theta$, and making the proper substitutions to obtain cosines in the first line and sines in the second, which will always be found possible, the equation will take the forms :—

$$\text{If } n \text{ is even, } 0 = \{ R_0 + R_2 \cos 2\theta + \dots + R_n \cos n\theta \} \\ - \{ r_2 \sin 2\theta + r_4 \sin 4\theta + \dots + r_n \sin n\theta \}.$$

$$\text{If } n \text{ is odd, } 0 = \{ R_1 \cos \theta + R_3 \cos 3\theta + \dots + R_n \cos n\theta \} \\ - \{ r_1 \sin \theta + r_3 \sin 3\theta + \dots + r_n \sin n\theta \}.$$

All the coefficients in these expressions are linear functions of the coefficients in the original equation which are readily determined.

The first line in either case is the projection of a line joining the first and last points of a linkage having 2θ as the external angle between the sides of the polygon, upon the line Ox .

The quantity within the bracket of the second line is the projection of another linkage having the same external angle 2θ , in its polygon, upon the line Oy .

The two trains may obviously be actuated *at once from the same first kite*.

The criterion derived from the equation is that the two projections shall be equal. When this is the case in the proper motion of the system, the root of the equation is $\tan \theta$, θ being half the angle between the two homologous sides of two consecutive kites.

The line joining the feet of the perpendiculars of projection must make an angle of -45° with Ox .

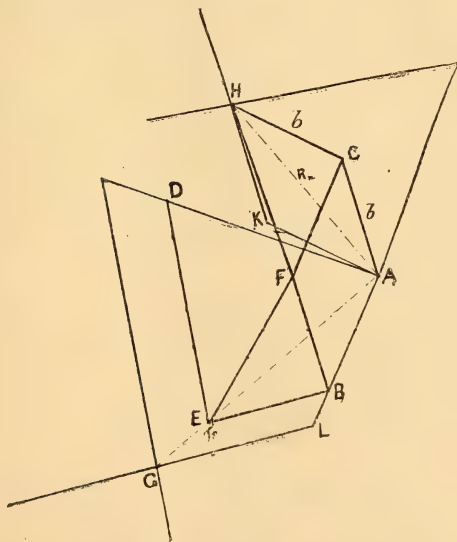
This does not constitute a very handy criterion, but it may be greatly improved in the following way.

In the first place, it is quite the same to the second linkage, so far as its projection and motion are concerned, whether it is actuated by the first by the proper connexion at the first or at the final chords of the polygons, or indeed at any parallel pair of chords, for each chord of the second or sine polygon is parallel to a corresponding chord of the cosine polygon, but the two have to be projected in directions at right angles one to the other.

If, therefore, the sine polygon can be bodily turned through an angle of -90° , it will then have to be projected in the same direction as the cosine polygon; and if the mechanism of connexion retains the extremities of the polygons together, and at the same time maintains the required proportionality among the chords generally, the criterion will simply amount to finding the first point of the sine polygon, now the final point of the whole train, in the line Oy .

The appropriate connexion is indicated in fig. 4. R_n, r_n

Fig. 4.



are the two chords, having their extremities together, and maintained in that condition by a pin common to the two kites, which have to be maintained at right angles.

If the vertices of the smaller isosceles triangles are as in
Phil. Mag. S. 6. Vol. 23. No. 138. June 1912. 3 N

the sketch, not both within the right angle, complete the small rhombus of one of them by adding the short bars bb .

Also take AB equal to b , and AD equal to a , the two sides of the last cosine kite. Between D and B insert the bars DE , EB , equal respectively to a and b . Complete the rhombus $BACF$ with bars, and join FH , FE with bars each equal to $\sqrt{2} \cdot b$.

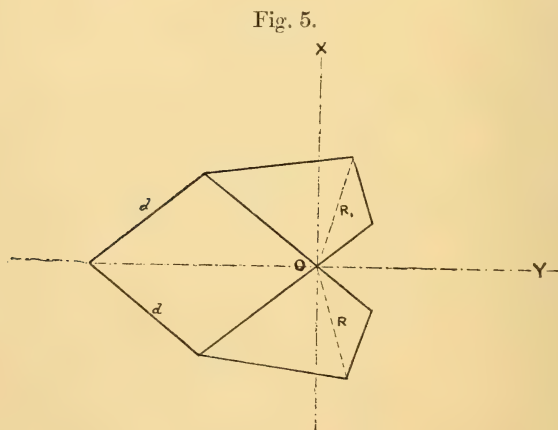
Then AE will be always equal to AH , and at right angles to it.

The chord r_n of the sine linkage always bears the same relation to AE , and therefore also to AH which is R_n .

The proof of this construction is seen at once by noting that the outlining bars of the figure $A-B-E-F-H-C-A$, with the additional links FB , FC , constitute a Sylvester pantograph of the form in which the ratio of the radii is one of equality, and the angle between them 90° .

In the case of n being even, sufficient expression has been given to the method to be observed; but when n is odd the first chord R_1 makes an angle of θ only with Ox , whereas the common angle between the chords externally is 2θ .

To secure that R_1 shall be maintained at the proper angle, add to the system a kite equal in all respects to the first and preceding it (fig. 5). Connect by two equal bars d either



the heads or tails of the two kites, and joining these bars by a joint at their other extremities, maintain the point of junction in the line of reference Oy . The motion will then be as desired.

It is not necessary that a problem should be stated as an

equation to be solved, in order to apply these Lazytongs methods, though, of course, every linkage equation implies one of the more ordinary sort in terms of powers of an unknown quantity, and the problem might have been stated in that form.

In the so-called problem of "doubling the cube" what is meant is, that a cube of edge a being given, the edge b of a cube of double the volume of the first shall be found.

Here $\frac{a^3}{b^3} = \frac{1}{2}$, and b is required. As a is less than b write $\frac{a}{b} = \cos \theta$, whence $\frac{a^3}{b^3} = \cos^3 \theta = \frac{1}{2}$.

The value of $\cos^3 \theta$ in cosines of multiples of θ is

$$\frac{\cos 3\theta + 3 \cos \theta}{4},$$

which, therefore, is to be equated to $\frac{1}{2}$ by the terms of the problem, and leads at once to the form adapted to linkage treatment:

$$0 = 2 - 3 \cos \theta - \cos 3\theta,$$

from which $\cos \theta$ or $\frac{a}{b}$ can be found. R_2 is in this case zero, and the linkage will accordingly require the treatment indicated in fig. 3.

The insertion of two mean proportionals between a the smaller and b the larger of two straight lines is one very nearly the same as the last. If x_1, x_2 are the two magnitudes required, and $\frac{a}{x_1} = \cos \theta$, then $\frac{a}{x_2} = \cos^2 \theta$, and $\frac{a}{b} = \cos^3 \theta$.

Therefore

$$\frac{a}{b} = \frac{\cos 3\theta + 3 \cos \theta}{4},$$

or

$$0 = 4 \frac{a}{b} - 3 \cos \theta - \cos 3\theta,$$

indicating the linkage required, one of the first sort. If, however, we make $\frac{a}{x_1} = \tan \theta$, $\frac{a}{x_2} = \tan^2 \theta$, $\frac{a}{b} = \tan^3 \theta$, we are no longer under the necessity of taking $\frac{a}{b}$ as less than

unity, but the linkage resulting will be of the second sort, and will be indicated by the equation :

$$0 = \{3a \cos \theta + a \cos 3\theta\} - \{3b \sin \theta - b \sin 3\theta\}.$$

In this case $\tan \theta = \frac{a}{x_1}$, $\tan^2 \theta = \frac{a}{x_2}$, when θ has been found by the linkage.

The trisection of the area contained between the hyperbola whose semiaxes are a and b , its semiaxis a , and a radius vector drawn from its centre to a point whose abscissa is x_3 , by other straight lines drawn through the centre, may be effected by a linkage.

Let x_1 and x_2 be the abscissæ of the points of the curve required by the problem, x_1 being smaller than x_2 .

The area of such a figure is equal to the quantity $\frac{a \cdot b}{2} \cdot \phi$, in which ϕ is a quantity such that $x = a \cosh \phi$, $y = b \sinh \phi$.

The problem, so far as x_1 is concerned, therefore amounts to finding $\cosh \phi$ when $\cosh 3\phi$ is given, for then $\frac{x_1}{a} = \cosh \phi$, when $\frac{x_3}{a} = \cosh 3\phi$. $\cosh 3\phi$ can be expressed in powers of $\cosh \phi$, thus: $4 \cosh^3 \phi - 3 \cosh \phi$.

Now $\cosh \phi$ can be always represented by $\frac{1}{\cos \theta}$. Hence

$$\frac{x_3}{a} = \frac{4}{\cos^3 \theta} - \frac{3}{\cos \theta},$$

$$\text{or} \quad 4 - 3 \cos^2 \theta - \frac{x_3}{a} \cos^3 \theta = 0;$$

whence in cosines of multiples of θ

$$0 = 10 - 3 \frac{x_3}{a} \cos \theta - 6 \cos 2\theta - \frac{x_3}{a} \cos 3\theta.$$

This formula indicates the linkage to be employed to find $\cos \theta$. It is of the first sort. When this cosine is determined, $x_1 = \frac{a}{\cos \theta}$, x_2 is found directly from x_1 from the equations

$$x_2 = a \cosh 2\phi, \quad x_1 = a \cosh \phi,$$

from which

$$x_2 = \frac{2x_1^2 - a^2}{a}.$$

XC. *A Theory of the Absorption and Scattering of the α Rays.* By C. G. DARWIN, B.A., Lecturer in Mathematical Physics, Manchester University*.

PART I.—ABSORPTION.

THE α particles from radioactive substances have been very thoroughly investigated, so that the main features of their motion are now well known. On account of their great mass they go straight or nearly straight through matter until their energy is exhausted. It is for this reason principally that an experimental formulation of their law of motion is comparatively so much easier than for the β rays. Bragg† showed that the number of α rays remained constant after traversing matter and that the absorptive effect was to be attributed to changes of velocity; and Geiger‡ found the form of the velocity curve§, which for mica he empirically represented by the equation $v^3 = V^3 (1 - x/R)$, where V is the initial velocity and R is the “range.” The present paper is concerned with the theoretical reason for this curve and the deductions which may be made from it. It also considers, but less completely, the scattering of the α particles.

§ 1. *The Mechanism of Absorption.*

It is known that the ionization produced by an α particle is proportional to the rate at which it loses its energy. It is thus necessary to adopt a structure for matter such that the α particle pulls electrons out of the atoms containing them and in so doing loses velocity. I have taken the atomic structure proposed by Prof. Rutherford||. This supposes the atom to consist of a cluster of electrons held by an unknown field of forces round a central charge, which is of such amount as to neutralize them and which is supposed to be the seat of the mass of the atom. This structure presents fewer analytical difficulties in the present problem than any other, and there is strong experimental evidence for it in the large scattering of the α rays¶. The adoption of this

* Communicated by Prof. E. Rutherford, F.R.S.

† W. H. Bragg, *Phil. Mag.* vol. x. p. 318 (1905).

‡ H. Geiger, *Proc. Roy. Soc. A.* vol. lxxxiii. p. 505 (1910).

§ I call by the name “velocity curve” the curve whose ordinate is the velocity of the α rays and whose abscissa is the distance they have travelled from their source.

|| E. Rutherford, *Phil. Mag.* vol. xxi. p. 669 (1911).

¶ Rutherford, *loc. cit.*, and H. Geiger, *Manc. Lit. & Phil. Soc.* 1911.

system necessarily involves that the helium atom, which is formed from an α ray, has only two electrons, an assumption which appears reasonable when it is remembered that the α particle is expelled with enormous velocity from one atom and is perpetually undergoing violent collisions with others, so that it must be of a very simple nature. I proceed parallel with the alternative assumptions that the electrons are distributed in the atom (1) throughout the volume of a sphere round the centre and (2) over its surface.

In passing through an atom an α ray will exert forces on the centre and on all the electrons. It will set any charges it approaches in motion and may succeed in pulling an electron out of the atom. In doing so it will lose velocity, while the ejection of the electron will be equivalent to ionization. Now in the atom there is a complicated field of forces acting between the electron and the rest of the system. This field is quite unknown, but the ease of the occurrence of ionization by collision suggests that it is not very great. That is to say, while an α particle is passing an electron their mutual forces are very much greater than the forces on either of the rest of the atom. On account of its high velocity the α particle will spend a very short time near an electron, and *in considering the motion of the α particle* we shall commit no great error in neglecting the effects of the perturbation of the electron by the rest of the atom. With regard to the motion of the electron this need not at all be true. As soon as the α particle has passed, the predominating factor is the atomic field which may prevent the electron from escaping or may greatly reduce its velocity.

We therefore suppose that the α particle loses its velocity by setting in motion a cluster of electrons whose interactions are negligible. In actual atoms the electrons will probably be already in motion, but it is possible to show that such motion only affects the result by the ratio of the squares of the velocities of electron and α particle, and this may presumably be regarded as a small quantity.

In traversing matter some α particles encounter more atoms than others and go deeper into them. Thus after going a given distance the α particles will have straggled out, and some will be moving faster than others. I have not succeeded in finding the amount of this straggling in the present problem ; but it is possible to prove with considerable generality that the mean loss of velocity of the particles after a given number of collisions is equal to the sum of the mean losses in each collision, a proposition which is not self-evident. It is this fact which makes the problem

of absorption much easier than that of transverse scattering, which is really more akin to straggling. In the scattering there is a considerable effect due to the inequalities and irregularities of distribution of the electrons. In the longitudinal motion such irregularities only affect the straggling and produce no change in the mean. The reason for this lies in the fact that here the composition of the effects of successive atoms is by simple addition, while for scattering it is by addition of squares.

§ 2. The Velocity Curve*.

If E, M, e, m be the charges and masses of α particle and electron; if $k = m/M$ and $\lambda = (1+k)Ee/m$, and if v be the velocity with which an α particle approaches an electron on a line at distance p from it, then a simple calculation of their orbits shows that after the two have separated the velocity of the α particle is $v + \Delta v$ where

$$(v + \Delta v)^2 = v^2(1 + 2k \cos 2\mu + k^2)/(1 + k)^2 \quad . \quad . \quad (1)$$

if $\tan \mu = \lambda/pv^2$. The α particle is deflected through an angle ψ where

$$\tan \psi = k \sin 2\mu / (1 + k \cos 2\mu) \quad . \quad . \quad . \quad (2)$$

These formulæ are accurate, whatever the values of m and M . But m is the mass of an electron so that k is small and (1) may be rewritten as

$$\Delta v = -kv(1 - \cos 2\mu) = -2kv \frac{\lambda^2/v^4}{p^2 + \lambda^2/v^4} \quad . \quad . \quad (3)$$

This is the velocity which the α particle loses in passing a single electron. In summing the effects of all the electrons of the atom, we encounter the difficulty that the forces exerted between an electron at one side of an atom and the particle at the other are not greater than the internal forces of the atom. In such a case, however, (3) gives a very small value, so that practically it is only the electrons very near the path of the α ray which contribute sensibly to the reduction of its velocity. It seems that the inclusion of all the electrons in the atom is less objectionable than the fixing of an arbitrary limit beyond which no forces shall be allowed to count†. Let n be the number of electrons in the atom.

* For a definition of this term see p. 901, note §.

† I originally worked out the whole theory, supposing that only electrons in a cylinder near the path of the particle exerted any force on it. The results are almost identical with the present.

We shall first find the result supposing the electrons distributed uniformly inside a sphere of radius σ_1 and afterwards supposing them arranged over the surface of a sphere of radius σ_2 . The numbers 1 and 2 subscribed will refer throughout to these alternative hypotheses.

Let P denote the distance from the centre of the atom of the initial line of motion of the α particle. In passing through the atom this line is slightly changed and the velocity is reduced, but the effects are small, and no error is produced by supposing the velocity on approaching each electron equal to the velocity of approach to the atom, and by supposing the line of motion through the atom to be straight. Let the position of an electron be denoted by cylindrical polar coordinates r, ϕ, z . The loss of velocity due to an electron at r, ϕ, z is

$$2kv \frac{\lambda^2}{v^4} \int \frac{\lambda^2}{v^4} + P^2 + r^2 - 2Pr \cos \phi,$$

and the chance of there being an electron at this point is

$$n_1 \int \frac{4}{3} \pi \sigma_1^3 \cdot r dr d\phi dz.$$

The whole loss of velocity on the average thus is:—

$$2kv \frac{\lambda^2}{v^4} \frac{n_1}{4/3\pi\sigma_1^3} \int_0^{\sigma_1} r dr \int_{-\sqrt{\sigma_1^2-r^2}}^{\sqrt{\sigma_1^2-r^2}} dz \int_0^{2\pi} d\phi \left/ \frac{\lambda^2}{v^4} + P^2 + r^2 - 2Pr \cos \phi \right/.$$

This expression is to be averaged for all values of P . The result gives ρ_1 , the mean loss of velocity of a particle in traversing an atom. Then:—

$$\rho_1 = 2kv \frac{\lambda^2}{v^4} \frac{n_1}{4/3\pi\sigma_1^3} \int_0^{\sigma_1} \frac{2P dP}{\sigma_1^2} \int_0^{\sigma_1} r dr \int_{-\sqrt{\sigma_1^2-r^2}}^{\sqrt{\sigma_1^2-r^2}} dz \cdot \int_0^{2\pi} d\phi \left/ \left(\frac{\lambda^2}{v^4} + P^2 + r^2 - 2Pr \cos \phi \right) \right/.$$

Three of the integrations can be performed, and if $\sigma_1^2 v^4 / \lambda^2 = w_1$, the expression may be reduced to

$$\rho_1 = 2k \frac{v}{w_1} n_1 \left\{ \log(1+w_1) - f_1(w_1) \right\} \quad \cdot \quad \cdot \quad (4)$$

where

$$f_1(w) = \int_0^1 \frac{x^{3/2} dx}{\sqrt{\left(x - \frac{1}{w}\right)^2 + \frac{4}{w}}} \cdot \frac{2}{2 + \frac{1}{w} - x + \sqrt{\left(x - \frac{1}{w}\right)^2 + \frac{4}{w}}}.$$

The logarithmic term in ρ_1 is the more important. f_1 is the sum of elliptic functions of all three kinds.

In the case of a surface distribution of electrons the corresponding integral reduces to

$$\rho_2 = 2k \frac{v}{w_2} n_2 \left\{ \log(1 + w_2) - f_2(w_2) \right\} \quad . \quad (5)$$

where $w_2 = \sigma_2^2 v^4 / \lambda^2$ and

$$J_2(w) = \int_0^1 \frac{x^{1/2} dx}{\sqrt{\left(x - \frac{1}{w}\right)^2 + \frac{4}{w}}} \cdot \frac{2}{2 + \frac{1}{w} - x + \sqrt{\left(x - \frac{1}{w}\right)^2 + \frac{4}{w}}}.$$

This is an elliptic function similar to f_1 . For large values of w , f_1 and f_2 have limits $2/3$ and 2 respectively and may be expanded in inverse powers of $w^{1/4}$, that is in the inverse velocity. For smaller velocities it is necessary to evaluate them by means of Jacobi's θ functions.

Before finding the equation of motion of the α particle we must estimate the direct effect on it of the central charge. The accurate equation (1) is applicable for this, with modified values of e and m . If these modifications are denoted by accents, the loss of velocity due to the central charge is, when small, given by

$$\Delta v = - \frac{2k'v}{(1+k')^2} \frac{\lambda'^2}{\lambda'^2 + P^2 v^4}.$$

The cases of large deflexion and large change of velocity are so rare that they may be disregarded, as they do not affect the mean. The average loss of velocity from the central charge thus is

$$\rho' = \frac{2k'v}{(1+k')^2} \frac{\lambda'^2}{\sigma^2 v^4} \log \left(1 + \frac{\sigma^2 v^4}{\lambda'^2} \right).$$

Now the electrical charge e' is equal to ne and hence

$$\lambda' = n \frac{k}{k'} (1 + k') \lambda,$$

so that

$$\rho' = \frac{2kv}{w} n \cdot \frac{nk}{k'} \cdot \log \left\{ 1 + w \left/ \left(\frac{nk}{k'} \right)^2 (1 + k')^2 \right. \right\}.$$

Now nk/k' is the ratio of the mass of all the electrons to that of the central charge, and this is quite a small quantity unless n is very large indeed; and we shall subsequently prove that this is not so. It is thus justifiable to neglect ρ' and take ρ as the mean loss of velocity in the atom.

If the number of atoms in a cubic centimetre is N the mean free path for a fast moving particle is $1/N\pi\sigma^2$. If v is the velocity at a distance x from the source we have

$$\frac{1}{N\pi\sigma^2} \frac{dv}{dx} = -\rho,$$

so that if V is the initial velocity

$$N\pi\sigma^2 x = \int_v^V \frac{dv}{\rho}.$$

Putting in the value of ρ found for either volume or surface distribution of electrons, this gives :

$$\begin{aligned} 8\pi k N n \sigma^2 x &= \int_v^V 4 \frac{w}{v} \frac{dv}{\log(1+w) - f(w)} \\ &= \int_{\sigma^2 v^4/\lambda^2}^{\sigma^2 V^4/\lambda^2} \frac{dw}{\log(1+w) - f(w)} \\ &= \int_{\log\left(1 + \frac{\sigma^2 v^4}{\lambda^2}\right)}^{\log\left(1 + \frac{\sigma^2 V^4}{\lambda^2}\right)} \frac{e^u du}{u - f(e^u - 1)}. \end{aligned}$$

For either subscript we shall put

$$\int_1^z \frac{e^u du}{u - f_{1,2}(e^u - 1)} = E_{1,2}(z).$$

Except for a constant the functions E_1, E_2 are very similar to the integral-exponential function Ei ; indeed, for large values of z they only differ by this constant from $e^a Ei(z-a)$ where $a_1 = 2/3$ and $a_2 = 2$.

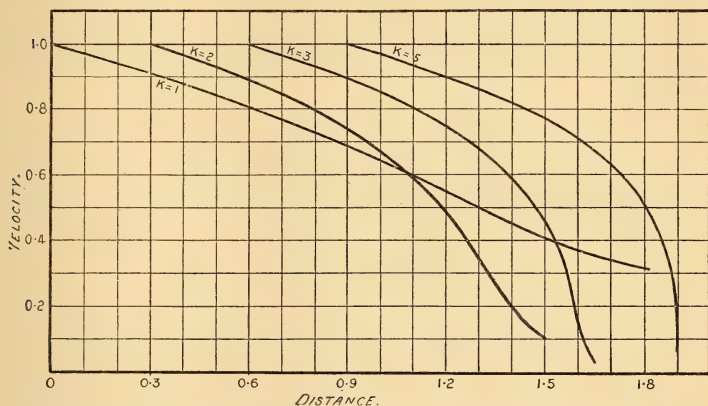
The velocity curve of the α particles thus is :—

$$8\pi k N n \sigma^2 x = E \log\left(1 + \frac{\sigma^2 V^4}{\lambda^2}\right) - E \log\left(1 + \frac{\sigma^2 v^4}{\lambda^2}\right) \quad \dots \quad (6)$$

It is interesting that the form of the curve should depend on the whole number of electrons in a cubic centimetre, and on the radius of the atom, but not at all on the number of atoms or the number of electrons in each atom. For very high velocities the curve is of the form $1-x = Av^4/\log v$. With different substances σ will be different and will make the shape of the curve vary. To consider this we write it in the form

$$1-x = E \log(1 + 10^k y^4) / E \log(1 + 10^k)$$

and call κ the parameter of the curve. It depends on σ and V and is taken in this form to facilitate the use of logarithms. The functions E_1, E_2 were evaluated by quadrature. The velocity curve obtained from E_1 is shown in the figure for



To avoid confusion each curve has been started 0.3 from the last.

parameters 1, 2, 3, 5. Those for E_2 are almost indistinguishable on the scale of the drawing. The curve for $\kappa=3$ is within $\frac{1}{2}$ per cent. of the curve $y^3=1-0.99x$ from $x=0$ to $x=0.95$, which is well within the experimental errors. That for $\kappa=2$ is nearly as good but diverges rather more at the end. For parameters greater than 2 it will be seen that the curve of velocity falls very steeply near $x=1$, and this corresponds to the existence of a range, which is so important a feature of the motion of the α rays. As the velocity diminishes there comes a point of inflexion and the final loss of velocity is exponential. Actually this part probably does not exist, as the α particles, which are straggling considerably, will undergo large deviations frequently, and it is very likely will pick up charges and become common gas molecules.

Equation (6) is thus capable of qualitatively representing the motion of the α rays. A great danger of basing a theory to account for experiments on a given law of force of the elementary parts, is that the supposed mechanism should not be the only one capable of accounting for the phenomena. This has caused trouble in such matters as viscosity, surface tension, etc. It would be hard, in the present case, to show that no other law of force could produce the same velocity curve, but that the curve cannot be obtained by merely supposing the α particles to surge through the atom with any

law of force may be proved by taking the only other simply soluble case, the inverse cube. Analytical difficulties enter a little earlier here, but when the velocity is very high it may be proved that the velocity curve is a common parabola, whereas with the inverse square it is $1-x=Av^4/\log v$. The difference is quite marked, and we may say that the results of experiment could not be deduced from any arbitrary law of force.

§ 3. *Application to Air.*

We next examine the velocity curve numerically. If the range of the α particles is R we have :—

$$8\pi N n k \sigma^2 R = E \log \left(1 + \frac{\sigma^2 V^4}{\lambda^2} \right) (7)$$

provided that $\log_{10} \sigma^2 V^4 / \lambda^2$, the parameter of the curve, is great enough to admit the existence of a range. We shall apply (7) to the case of RaC in air, as it is with this substance that most of the experiments have been made. The mean range is 6.8 cm. and the initial velocity 2.0×10^9 cm. per sec. The quantities $N = 5.44 \times 10^{19}$, $k = 1.37 \times 10^{-4}$, $E = 9.3 \times 10^{-10}$ (ES), and $e/m = 5.31 \times 10^{17}$ (ES) are all directly known from various experiments. σ , the radius of the atom, is a more difficult matter. A value can be assigned from the kinetic theory of gases, but this need not be at all the same as the value required here. For the kinetic theory determines the mean distance of closest approach of two molecules in collision. Here we require the mean radius of the atom at all times. It is possible to suppose the atom highly compressible, so that the electrons are usually at a considerable distance from the centre, but are driven back on it by the approach of a second molecule. Or we may suppose them held very close to the centre, but capable of exerting outside their region large elastic forces on other atoms. In the first case σ will be larger, in the second smaller than the value given by the kinetic theory, which moreover refers to molecules, not atoms. If the atom of air is highly compressible its radius will be say 3×10^{-8} cm. This would give for RaC a parameter $\kappa = 4.8$, which is almost certainly too large. Moreover, it would result from compressibility that the mean radius would depend somewhat on the pressure; but the stopping of the α rays depends only on the number of atoms it encounters, and not at all on their pressure. This possibility may therefore be rejected, and to cover the other

I proceed by assuming for σ the three values 10^{-8} , $10^{-8.5}$, 10^{-9} cm. The last is very small, the reason why it is included will appear in the discussion of the motion of the α particles through hydrogen. With these three values the parameters of the velocity curves are 3.82, 2.82, and 1.82, all values which would give a curve resembling fairly closely the experimental curve. There is now only one unknown in (7) and by solving we can find the value of n . In the three cases I find for volume distribution $n_1 = 7.4$, 11.1, 19.2, and for surface $n_2 = 8.7$, 13.2, 22.7. Thus, although σ is very uncertain, it appears that n is somewhere near the atomic weight. The slow variation of n_1 and n_2 with σ is due to the fact that for these parameters E_1 and E_2 are approximately

$$\frac{\sigma^2 V^4}{\lambda^2} \bigg/ \log \frac{\sigma^2 V^4}{\lambda^2},$$

so that σ only appears in (7) by its logarithm. These values of n are in good agreement with those determined by other methods; in particular, Rutherford * found the number of electrons as half the atomic weight from experiments on large scattering of the α rays. Some of the other determinations of n are on hypotheses contrary to the present, so that for these confirmation is meaningless.

§ 4. Applications to other Substances.

We must next examine the absorption under other conditions. Any mechanical hypothesis would give the correct law for variations of pressure and for compound substances. We need therefore only consider elements. In doing so it is not convenient to consider the whole range in each substance, as the end of the range can only be observed in a gas and also because it fails to convey part of the information which can be obtained. We take, as do experimenters, air as a standard, and compare the absorbing powers of thin layers of various elements with those of air. If we denote by accents the various quantities pertaining to the substance to be examined, the α particle in this substance will lose a velocity Δv in a length $\Delta x'$ where

$$\Delta v = N' \pi \sigma'^2 \Delta x' \cdot 2k \frac{\lambda^2}{\sigma'^2 v^3} \left\{ \log(1 + w') - f(w') \right\}$$

where as always $w' = \sigma'^2 v^4 / \lambda^2$. The same velocity is lost in a distance Δx of air, where

$$\Delta v = N \pi \sigma^2 \Delta x \cdot 2k \frac{\lambda^2}{\sigma^2 v^3} \left\{ \log(1 + w) - f(w) \right\}.$$

* Rutherford, *loc. cit.*

By division then :—

$$\frac{\Delta x}{\Delta x'} = \frac{N'n' \log(1+w') - f(w')}{Nn \log(1+w) - f(w)} \quad \dots \quad (8)$$

Then Δx is the "air equivalent" of a film of thickness $\Delta x'$ of the substance. (8) shows why equivalence should depend on the velocity of the α rays. By means of (8) we might theoretically solve and find all the atomic constants including the radius of the air atom. For if the equivalent of $\Delta x'$ is known at three different velocities, then two equations can be formed involving σ and σ' , and can be solved. (7) then gives n and (8) n' . I have attempted such a solution for gold, but the values of σ and σ' which were obtained were certainly too small to be admissible. The data used were taken from some experiments by Taylor*, who records the equivalence of a certain gold foil at various velocities. He measured the velocity by finding the range which the α rays still had to run after passing the foil. This method of determining equivalence is open to the objection that it is not quite certain what is the quantity that is measured. The ionization falls off very rapidly at the end of the range and so very accurate measurements of change of range can be made. But the shape of the curve at the end depends largely on the amount of the straggling among the α rays, and this will vary systematically from one substance to another. Hence measurements at the end of the range need not give at all accurately the velocity at an earlier point, and we must abandon the hope of a complete direct solution.

By supposing σ known for air we need only use two measurements, and these may be taken fairly close together so as to minimize the effect of change of shape of the ionization curve. If Δx_1 , Δx_2 are the distances in air equivalent to $\Delta x'$ at velocities v_1 , v_2 , then from (8) we have

$$\frac{\Delta x_1}{\Delta x_2} = \frac{\log(1+w_1') - f(w_1')}{\log(1+w_1) - f(w_1)} \frac{\log(1+w_2) - f(w_2)}{\log(1+w_2') - f(w_2')} \quad \dots \quad (9)$$

To solve this for σ' we ought, strictly speaking, to determine the velocities v_1 , v_2 from the recorded ranges by the velocity curve itself, but it is easy to see that the empirical formula $v^3 = V^3(1-x/R)$ is quite accurate enough. The solution of (9) determines w_1' and w_2' . (8) then gives n' . The solutions all depend on the value assumed for σ the radius of the air atom. Table I. gives the solutions for the substances which Taylor† examined. The numbers in each column all depend on the value taken for the first row. For

* T. S. Taylor, Phil. Mag. vol. xviii. p. 604 (1909). The numbers used were extracted from Tables I. and II.

† Taylor, *loc. cit.*

TABLE I.

 n is the number of electrons in the atom. σ is the atomic radius. κ is the parameter of the velocity curve. $\Delta x'$ is the thickness of the film. Δx_1 is the equivalent in air at range 5.7 cm. Δx_2 " " " 3.7 cm. Δx_3 " " " 2.1 cm.

For Al the change of equivalence is very slow and so the range 2.1 cm. was used for the solution and the range 3.7 cm. for comparison. For H, Δx_1 is at range 5.2 cm. and Δx_2 at range 4.0 cm.

Data used for the solutions.

	$\Delta x'$.	Δx_1 .	Δx_2 .	Δx_3 (obs.).	Δx_3 (calc.).
Au	1.27×10^{-4}	.719	.657	.600	.570
Pb	2.84×10^{-4}	1.104	.999	.888	.853
Sn	3.86×10^{-4}	1.011	.957	.882	.877
Al	3.30×10^{-4}	.597	.584	.597	.592
H	1.07	.231	.247		

Volume Distribution.				Surface Distribution.		
Air	σ .	10^{-8}	$10^{-8.5}$	10^{-8}	$10^{-8.5}$	10^{-9}
	n .	7.4	11.1	8.7	13.2	22.7
	κ .	3.82	2.82	3.82	2.82	1.82
Au	σ .	10.0×10^{-10}	6.9×10^{-10}	4.0×10^{-10}	9.0×10^{-10}	6.1×10^{-10}
	n .	89	117	182	113	152
	κ .	1.82	1.49	1.01	1.72	1.38
Pb	σ .	8.8×10^{-10}	6.2×10^{-10}	3.7×10^{-10}	7.8×10^{-10}	5.4×10^{-10}
	n .	106	140	215	137	182
	κ .	1.70	1.40	.95	1.61	1.28
Sn	σ .	17.8×10^{-10}	10.7×10^{-10}	5.3×10^{-10}	16.6×10^{-10}	9.7×10^{-10}
	n .	48	65	104	60	82
	κ .	2.32	1.88	1.27	2.26	1.79
Al	σ .	6.7×10^{-9}	2.5×10^{-9}	0.90×10^{-9}	6.6×10^{-9}	2.4×10^{-9}
	n .	13.2	19.2	32.5	15.5	23.1
	κ .	3.47	2.62	1.72	3.46	2.60
H	σ .			4.3×10^{-8}		6.7×10^{-8}
	n .			.99		1.01
	κ .			5.1		5.5

each substance a row is devoted to the parameter (for particles from RaC). In some cases it appears very small, but this is implicit in the experiments, which show a great difference in the characters of the various velocity curves. In the case of hydrogen (9) is insoluble for the two larger values of σ . This means that with these values the relation between the air velocity curve and that of hydrogen is such that the latter is a more abrupt curve than would be one with an infinite parameter. The first part of the table gives the data used for the solutions. In addition to the atomic constants σ and n , I also calculated for comparison with experiment the equivalent of the film at a third velocity. Within narrow limits this came out the same for all six columns, which means that an enormous change must be made in σ before any appears in Δx_3 . This shows that it would be impossible to get measurements of sufficient accuracy to determine the radius of the air atom in addition to the other constants, the theoretical possibility of which is indicated above.

The table shows that n is proportional to the atomic weight for the heavier substances. Hydrogen is in conformity with this, when the solution exists. It is clear, however, from the great difference between σ for surface and σ for volume distribution (which, when there is only one electron in the system, cannot correspond to any very great physical difference) that our analysis cannot be regarded as holding for systems containing a very small number of electrons. It is probably the assumption that the α particle exerts no force except when inside a sphere *round the centre*, which breaks down. Since the result with regard to σ is certainly unsatisfactory, it is very doubtful how much significance is to be attached to the value for n . The absence of the hydrogen solution for larger values of σ for air may also be due to the inapplicability of our analysis to the case of a very small number of electrons. If this larger value of σ for air is adopted, then for air and the metals n will be about half the atomic weight and hydrogen will be exceptional; if the small value of σ be taken, then n will be equal to the atomic weight and hydrogen (as far as the analysis is to be trusted for it) will be regular. In this case helium will be exceptional, for the whole hypothesis depends on the assumption that for it $n=2$. Great importance thus attaches to the case of helium, because there is only one adjustable constant σ instead of two, σ and n . Unfortunately no measurements of equivalence have been made, but only a determination of the whole range*. If the value found for this be put in (7)

* E. P. Adams, *Physical Review*, vol. xxiv. p. 108 (1907).

and the equation be solved for σ , a value is given several times greater than 10^{-8} . Thus here as for hydrogen σ has a value greater than that given by the kinetic theory, and this may probably be set down to the inaccuracy of meaning of σ in the case of a very small number of electrons in the atom.

From the table it appears that as the atomic weight grows σ becomes less and is very small for a heavy substance. This is rather surprising, but it does not seem unreasonable that a small cluster of a large number of electrons should exert elastic forces at as great a distance as a larger cluster composed of a smaller number. There is no great difference which should enable us to distinguish whether the distribution of electrons through the volume of the atom or that over its surface gives values most in agreement with the results of experiment.

The fact that stopping power depends on both n and σ prevents the deduction of any simple relation from Bragg's law of stopping power*. Table I. suggests that n is proportional to the atomic weight A , and if this is supposed accurately true it is possible to find a relation for σ ; but it is not very intelligible because it contains the velocity, and it was only by neglecting the variation due to velocity that Bragg propounded his law. The "atomic stopping power" of Bragg is, from (8), proportional to $n'\{\log(1+w')-f(w')\}$ and this is proportional to $\sqrt{A}$. Then approximately $\log w'$ varies as $1/\sqrt{A}$, or making the velocity constant

$$\log \sigma' + \text{const.} \propto 1/\sqrt{A},$$

which is the form that Bragg's law takes on the present theory.

The analysis of this paper is not sufficient to give a complete figure of the Bragg ionization curve. In the earlier part of the range the ionization is proportional to the mean rate of loss of energy of the α rays. But the interesting part of the curve is the end, and here measurement of loss of energy is useless, because the dominant factor is the straggling of the rays, and the problem of this straggling has not been discussed. In his investigation on the connexion between ionization and absorption, Geiger points out that the ionization is inversely proportional to the velocity of the rays. On the present hypothesis this is accidental. If the ionization is proportional to the rate of

* W. H. Bragg, *loc. cit.*

expenditure of energy, and if the velocity curve is approximately $v^3 = V^3(1 - x/R)$, then it follows directly that the ionization is approximately inversely proportional to the velocity; and no further significance need be attached to this relation.

PART II.—SCATTERING.

The mechanism which accounts for absorption must also be capable of accounting for scattering. The problem of scattering is the more complicated of the two, as it deals not with a mean effect, but with the mean departure from such an effect, and in this way is analogous to the problem of straggling rather than to that of absorption. In consequence of this difference, difficulties enter which prevent the complete solution, and we must be satisfied with an approximation.

§ 5. *The Formulæ for the Scattering.*

The difficulty of the scattering lies in the fact that when an electron lies very close to the path of the particle it exerts a much greater effect than the average, and this effect is not counterbalanced by the absence of an electron in succeeding encounters. In the case of the absorption, any effect of such an electron does not alter the mean, but only tells on the amount of straggling. To consider the scattering it is thus convenient to divide the effect of the atom into two parts. The first is due to the regular average distribution of electrons together with the effect of the central charge. The combined effect of these is a deflexion in a plane through the centre. The second is due to the chance occurrence of electrons very near the path of the α particle. This deflexion will be in an arbitrary direction.

(i.) The deflexion by a single electron is from (2) equal to $2k \frac{\lambda p v^2}{\lambda^2 + p^2 v^4}$. The component of this expression in a plane through the centre of the atom is to be summed for all the electrons. In this summation the electrons very near the path of the particle will contribute equal amounts in all directions, so that there is no need to exclude them on the ground that they are to be counted later. The summation of all the electrons, and the averaging for all positions of the α particle, gives, as in the case of the absorption, a quadruple

integral. The mean deflexion from the electrons is

$$\psi_1' = \frac{2kn_1}{4/3\pi\sigma_1^3} \int_0^{\sigma_1} \frac{2PdP}{\sigma_1^2} \int_0^{\sigma_1} r dr \int_{-\sqrt{\sigma_1^2 - r^2}}^{\sqrt{\sigma_1^2 - r^2}} dz \int_0^{2\pi} d\phi \frac{\lambda/v^2(P - r \cos \phi)}{\lambda^2/v^4 + P^2 + r^2 - 2Pr \cos \phi}.$$

Only two of the integrations can be performed, and the expression then becomes elliptic and progress would be difficult. We shall at once evaluate it on the supposition that $\sigma^2 v^4/\lambda^2$ is large, as the development of (ii.) later is only possible with large velocity. In this case

$$\psi_1' = 2k \frac{n_1 \lambda}{\sigma_1 v^2} \left(2 - \frac{3}{8} \pi \right).$$

In the case of a surface distribution a similar process gives

$$\psi_2' = 2k \frac{n_2 \lambda}{\sigma_2 v^2} \left(2 - \frac{1}{2} \pi \right).$$

The central charge plays a large part in scattering through small angles as well as through large. From (2) the deflexion is ψ'' where

$$\tan \psi'' = 2k' \lambda' P v^2 / P^2 v^4 (k' + 1) - \lambda'^2 (k' - 1),$$

When $k' > 1$ this quantity can take any value positive, negative, or infinite. In experiments on small scattering when a large deflexion occurs, the α particle does not appear on the field of observation. Suppose that a particle which is deflected through an angle greater than δ is not observed. δ will be of the order of 2° or 3° . This excludes from the mean to be taken values of P less than a certain amount. For larger values of P , ψ'' may replace its tangent. When the mean is taken it appears that when the velocity is high the part dependent on δ is unimportant and that the mean is given by neglecting the second term of the denominator,

$$\text{Thus} \quad \psi'' = 4 \frac{\lambda'}{\sigma v^2} \frac{k'}{k' + 1} = 4 \frac{k \eta \lambda}{\sigma v^2}.$$

ψ'' is away from the centre, ψ' towards it. Hence their combined effect is

$$\psi'' - \psi_1' = 2k \frac{n_1 \lambda}{\sigma_1 v^2} \frac{3}{8} \pi$$

for volume, and

$$\psi'' - \psi_2' = 2k \frac{n_2 \lambda}{\sigma_2 v^2} \frac{1}{2} \pi$$

for surface distribution. Here for the first time there enters a distinct difference between the effects of the alternative distributions,

(ii.) Sir J. J. Thomson * has shown how to deal with the irregular deflexions due to electrons lying very close to the path of the α ray. The present is a modification of his method to suit the hypotheses of this paper. Suppose that any electron in a cylinder of radius l round the path is to be counted as very near it. The mean deflexion of such an electron is

$$2k \frac{\lambda}{v^2} \cdot \frac{2}{l} \left\{ 1 - \frac{\lambda}{lv^2} \tan^{-1} \frac{lv^2}{\lambda} \right\}.$$

When v is large the second term is negligible, and unless this is so progress is prevented, since l will not disappear from the equation and it is impossible to know what is the right value to take for l . To estimate the whole effect of all the electrons in the cylinder we must multiply this expression by the square root of their number. For volume distribution their number is

$$n_1 \pi l^2 \cdot 2 \sqrt{\sigma_1^2 - P^2} \Big/ \frac{4}{3} \pi \sigma_1^3,$$

and the mean of the square root of this for all values of P is

$$\frac{l}{\sigma} \frac{4}{5} \sqrt{\frac{3}{2}} n.$$

Thus the whole deflexion due to these electrons is

$$\psi_1''' = \frac{4k\lambda}{\sigma_1 v^2} \sqrt{n_1} \frac{4}{5} \sqrt{\frac{3}{2}}.$$

The corresponding expression for surface distribution is

$$\psi_2''' = \frac{4k\lambda}{\sigma_2 v^2} \sqrt{n_2} \frac{4}{3} \sqrt{\frac{1}{2}}.$$

These deflexions are in arbitrary directions and must be compounded with those of (i.). The results are ψ_1 , ψ_2 the mean deflexion of the whole atom.

$$\begin{aligned} \psi_1 &= \frac{2k\lambda}{\sigma_1 v^2} \left\{ \left(\frac{3}{8} \pi n_1 \right)^2 + \left(\frac{8}{5} \sqrt{\frac{3}{2}} n_1 \right)^2 \right\}^{1/2} \\ &= \frac{k\lambda n_1^{1/2}}{\sigma_1 v^2} \cdot \frac{3}{4} \pi \sqrt{n_1 + 2.77}; \quad . \quad . \quad . \quad (10) \end{aligned}$$

$$\begin{aligned} \psi_2 &= \frac{2k\lambda}{\sigma_2 v^2} \left\{ \left(\frac{\pi}{2} n_2 \right)^2 + \left(\frac{8}{3} \sqrt{\frac{1}{2}} n_2 \right)^2 \right\}^{1/2} \\ &= \frac{k\lambda n_2^{1/2}}{\sigma_2 v^2} \cdot \pi \sqrt{n_2 + 1.44}. \quad . \quad . \quad . \quad (11) \end{aligned}$$

* Sir J. J. Thomson, Proc. Camb. Phil. Soc. xv. pt. 5 (1910).

For high velocities the scattering should thus vary inversely as the square. The measurements of Geiger* on the dependence of scattering on velocity are not very accurate, but the inverse cube gave the best agreement. As this was determined with some quite low velocities, (10) and (11) may be regarded as reasonably satisfactory from this point of view.

The quantities ψ_1 , ψ_2 are mean angles of deflexion. Geiger measured the most probable angle. Assuming (as has already been tacitly done) an error law of distribution, the latter is obtained by multiplying ψ by $\sqrt{2/\pi}$.

It is convenient to consider both ψ_1 and ψ_2 together by writing them

$$\frac{k\lambda n^{1/2}}{\sigma v^2} \pi \nu,$$

where

$$\nu_1 = \frac{3}{4} \sqrt{n_1 + 2.77} \quad \text{and} \quad \nu_2 = \sqrt{n_2 + 1.44}.$$

For a thin foil the whole scattering is obtained by multiplying ψ by the square root of the number of atoms encountered. In a foil of thickness Δx this number is $N\pi\sigma^2\Delta x$ and the most probable angle of scattering is

$$\chi = \frac{k\lambda}{v^2} \pi n^{1/2} \nu \sqrt{2N\Delta x}. \quad . \quad . \quad . \quad (12)$$

Experiments on scattering at high velocities should thus be able to determine n without σ .

Geiger performed experiments with both small and great thicknesses of gold, but for other metals he only had thick foils, and for such the change of velocity during transit has to be taken into account. Geiger† has shown how this explains the shape of the curve connecting scattering with thickness of the scattering foil. I follow his method, but use my own formulæ as the result is rather simple. When the variation of velocity is taken into account the most probable angle of scattering is

$$\chi = k\lambda\pi n^{1/2} \nu \left\{ 2N \cdot \Sigma \frac{\Delta x}{v^4} \right\}^{1/2}.$$

Now

$$\Sigma N\pi\sigma^2\Delta x/v^4 = \int_v^V dv/\rho v^4,$$

where V and v are the incident and emergent velocities

* H. Geiger, Proc. Roy. Soc. A. vol. lxxxiii. p. 492 (1910).

† H. Geiger, Proc. Roy. Soc. A. vol. lxxxvi. p. 236 (1912).

of the rays. Putting in the value of ρ from (4) or (5) we have

$$\chi = \sqrt{k\pi v} \cdot \frac{1}{2} \left\{ \int_{\sigma^2 v^4 / \lambda^2}^{\sigma^2 V^4 / \lambda^2} \frac{dw}{w \{ \log(1+w) - f(w) \}} \right\}^{1/2}$$

Now ψ was obtained on the assumption that $\sigma^2 v^4 / \lambda^2$ is large, and so here the second factor of the denominator may be replaced by $\log w - a$, a being the limiting value of f , $2/3$ for f_1 and 2 for f_2 . When this change is made the integration can be performed and gives

$$\chi = \frac{1}{2} \sqrt{k\pi v} \sqrt{\log \frac{\frac{\sigma^2 V^4}{\lambda^2} - a}{\frac{\sigma^2 v^4}{\lambda^2} - a}} \quad \dots \quad (13)$$

§ 6. *Comparison with Experiment.*

Of the substances whose absorption has been discussed, Geiger* made experiments with gold, tin, and aluminium. I apply (13) to foils of these substances of thickness equivalent to 1 cm. of air, and I apply (12) to thin gold foils as well. The assumption that $\sigma^2 v^4 / \lambda^2$ is large is hardly justified for gold, especially for the values corresponding to a small radius of the air atom. Indeed for gold, even in the most favourable case an application of (13) to a thin foil gives a value differing by 10 per cent. from that deduced from (12), and (12) is only superior to (13) in that $\sigma^2 v^4 / \lambda^2$ has been supposed large once instead of twice.

Table II. gives, for comparison with the experimental

TABLE II.

Most probable Angles of Scattering.

	Observed.	Volume Distribution.			Surface Distribution.		
σ for air		10^{-8}	$10^{-8.5}$	10^{-9}	10^{-8}	$10^{-8.5}$	10^{-9}
1 Au foil	10'	13'	17'	27'	22'	30'	45'
2 " "	23'	19'	25'	38'	31'	42'	64'
Au equiv. to 1 cm. air ...	2°·1	1°·24	1°·63	2°·8	2°·63	4°·4	
Sn " " " ...	1°·5	0°·79	1°·05	1°·74	1°·43	2°·14	5°·9
Al " " " ...	0°·6	0°·35	0°·48	0°·80	0°·53	0°·79	1°·58

* H. Geiger, Proc. Roy. Soc. A. vol. lxxxiii. p. 492 (1910).

results, the values of the most probable angles of scattering deduced from the numbers in the six columns of Table I. For the thick foils (13) was used, for the thin (12). I have calculated the latter for both 1 and 2 foils, as Geiger's measurement with one foil seemed to be in not very good agreement with the next few.

Except for the last column the results are of the right order. The divergence of the last column is chiefly due to the fact that $\log w_2 - a_2$ does not then in the least approximate to $\log (1 + w_2) - f_2(w_2)$. In the case of gold indeed $\log w_2 - a_2$ changes sign. In spite of this divergency for the surface distribution expressions, which masks their true value, it does seem possible now to discriminate definitely in favour of the volume distribution, and it seems that the smaller values of σ are best. Since the closeness of the approximation of χ to its true value is unknown, it does not seem profitable to fix the value with any greater accuracy.

The agreement between the observed and calculated values for the scattering is thus good enough entirely to confirm the hypothesis of this paper, but not so good as to help much in a more accurate specification of the atomic constants.

Summary.

An hypothesis is put forward whereby the α particles in passing through matter pull electrons out of the atoms they traverse, acting on them with the ordinary law of the inverse square.

An equation is deduced relating their velocity to the distance they have travelled from their source. This is the "velocity curve" and agrees closely with the experimental curve.

The equation involves two unknown constants: n the number of electrons in each atom, σ the radius of the atom. In the case of air, if σ be assumed known, n can be deduced from the range. Widely different values of σ give very similar values of n .

From comparison of the stopping powers of air and other substances, σ and n for these can be deduced, the values all depending on the original value assumed for the radius of the air atom.

The number of electrons in the atom appears to be intermediate between the atomic weight and its half. The atomic radii decrease with increasing atomic weight.

In the case of hydrogen it seems probable that the formula for σ does not hold on account of there being only very few

electrons in the atom. If it is regarded as holding, then $n=1$ almost exactly, but σ is very much larger than seems probable. σ is also too large for helium, for which $n=2$.

The numbers obtained from absorption are applied to scattering and give results in all cases in very good agreement with experimental measurements.

My thanks are due to Professor Rutherford for the interest he has taken in this paper and for the advice with which he has helped me.

XCI. On the Deduction of Wien's Displacement Law.

By E. BUCKINGHAM *.

1. **A**LTHOUGH Wien's displacement law may be regarded as quite well established by experiment, its great importance seems to justify attempts to improve or simplify the reasoning by which it may be deduced *à priori* as a consequence of the general principles of thermodynamics and the electromagnetic theory of radiation. Any such deduction must, in substance, contain the following four elements :—

- (a) The treatment, by Doppler's principle, of the change of wave-length produced when diffuse radiation is compressed or expanded within a perfectly reflecting shell, *i. e.* adiabatically.
- (b) The evaluation, by means of the principle of the conservation of energy, of the change of the volume density of the radiant energy which occurs during the adiabatic change of volume and accompanies the change of wave-length. This step involves the use of the value of the pressure of diffuse radiation on a bounding surface, deduced from the electromagnetic theory and confirmed by experiment.
- (c) The demonstration, by means of the second law of thermodynamics, that black radiation remains black when its density and temperature are changed by adiabatic change of volume.
- (d) The use of the Stefan-Boltzmann law to correlate the results obtained by the steps (a), (b), and (c), so that the displacement law shall appear as a necessary consequence of those results.

These parts of the deduction need not be kept entirely separate, nor do they necessarily occur in the order given

* Communicated by the Author.

above, which is that followed in this paper, but they must be present in some form or other. In the deductions I have read, the treatment of the change of wave-length seems somewhat difficult or obscure, and I have attempted to simplify this part of the subject and make it easier to grasp. The remainder of the demonstration contains little that is at all novel, but is given for the sake of presenting a connected whole, comprehensible to those who are not already familiar with the subject. The treatment is elementary and relates only to radiation *in vacuo*.

2. Let ds be an infinitesimal plane element of surface at a point within a field of radiation. A certain amount of radiant energy passes through ds from the negative to the positive side, in unit time, in various directions. Let us consider only those directions comprised within a cone of the infinitesimal solid angle dw described about the positive normal to ds . The amount of energy of wave-lengths between λ and $\lambda + d\lambda$, which passes through ds from the negative to the positive side in one second, in directions close enough to the normal to lie within the cone, may be expressed by

$$R_{\lambda} d\lambda \cdot ds \cdot dw.$$

The quantity $R_{\lambda} d\lambda$ may be called the strength of the radiation, and R_{λ} the "radiant vector" at the given point, in the given direction of the positive normal to ds , and for the wave-length λ . If the value of R_{λ} is given for all values of λ , for all directions, and at every point within a given region, the radiation within that region is, for our purposes, completely specified, since questions of phase and state of polarization will not enter into our reasoning.

By speaking of "the energy of wave-lengths between λ and $\lambda + d\lambda$ " we make a somewhat violent though familiar assumption, namely, that no matter what may be the nature of the pulses which constitute radiation, since our spectral apparatus enables us to analyse radiation into series of wave-trains of assignable period, the radiation *before analysis* may be treated as the sum of these wave-trains coexisting independently. However obvious the truth of this assumption may appear from a purely mathematical standpoint, it is well to recognize that *physically* it is to be justified by the agreement with experiment of conclusions drawn from it. It is, in fact, thus justified and we shall make a rather full use of this principle.

3. Let us consider a closed evacuated shell, the walls of which reflect perfectly but at least somewhat irregularly.

Let a beam of approximately monochromatic radiation of wave-lengths between λ and $\lambda + d\lambda$ be admitted to the enclosure through a hole, which is then closed by a cover similar in its properties to the rest of the walls. After a short time the radiation within the shell becomes perfectly diffuse, for the directed quality of the original beam is soon obliterated by the successive irregular reflexions, so that thereafter the value of R_λ is the same at all points and in all directions. These reflexions, however, do not change the period of the radiation, since there is no absorption and remission but only pure reflexion. The volume-density of the energy is now

$$\rho_\lambda d\lambda = 4\pi \frac{R_\lambda d\lambda}{c}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where c is the velocity of light, and the whole amount of energy within the shell is $v\rho_\lambda d\lambda$, if v is the volume of the shell.

Let M be a small plane piece of the shell-wall of area s , and let M be given a normal velocity βc outward, β being infinitesimal. This motion will disturb the perfect diffuseness of R_λ by an amount which we shall show to be negligible, but at present we shall assume that R_λ remains diffuse.

The reflexion from M also causes a change of period, which we must now proceed to evaluate. If a wave-train of period T strikes M at an angle of incidence ϕ , it is easily seen that the period T' of arrival of the waves at a given point of M is

$$T' = \frac{T}{1 - \beta \cos \phi}.$$

The period at a point of the moving surface is therefore greater than at a fixed point in space in the ratio

$$r_a = 1 + \beta \cos \phi, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

terms of higher orders in β being negligible. A disturbance starting with the period T' at a point of the moving surface and propagated at an angle ψ with the normal has, upon arrival at a fixed point in space, the period

$$T'' = T'(1 + \beta \cos \psi),$$

so that the effect of departure is to increase the period in the ratio

$$r_d = 1 + \beta \cos \psi. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Our problem is to find the total effect on the original period T of all the arrivals and departures, at all possible angles ϕ

and ψ from 0 to $\pi/2$, during a long time t ; and to do this we must find the number of times that each of these effects is produced on every wave, *i. e.* every element of the radiation existing within the shell.

4. We base our reasoning on the consideration that in a very long time—though not in a short one—every element of the energy within the shell must undergo reflexion from M at the angles (ϕ, ψ) just as many times as every other element. The number of times that any particular effect of reflexion at M is produced on each element of the energy is therefore the ratio of the total amount of energy thus affected in the time t to the total amount present within the shell. The changes of period in the ratios r_a and r_d , caused by arrival and departure, occur alternately, and in finding the total effect of a number of successive arrivals and departures we have evidently to evaluate a product of the form

$$r_a r_d \cdot r_a' r_d' \cdot r_a'' r_d'' \dots \&c.$$

But since multiplication is commutative, we shall get the same result if we pursue the more convenient method of treating all the arrivals by themselves, then all the departures by themselves, and finally multiplying the two resulting ratios together to get the combined effect of both arrivals and departures.

We start, then, with the arrivals. In any time t the amount of energy which strikes M at angles between ϕ and $\phi + d\phi$ is

$$t \cdot R_\lambda d\lambda s \cos \phi \cdot 2\pi \sin \phi d\phi.$$

The total amount present within the shell to be affected is, by equation (1),

$$v \cdot \frac{4\pi R_\lambda d\lambda}{c}.$$

Hence the number of times n that each element of the energy arrives at M at angles between ϕ and $\phi + d\phi$ within the long time t is

$$\begin{aligned} n &= \frac{t \cdot R_\lambda d\lambda s \cos \phi \cdot 2\pi \sin \phi d\phi}{v \frac{4\pi R_\lambda d\lambda}{c}} \\ &= \frac{cts}{2v} \cos \phi \sin \phi d\phi \dots \dots \dots (4) \end{aligned}$$

By equation (2) the effect of all these n arrivals is to increase the period in the ratio

$$r_a^n = (1 + \beta \cos \phi)^n = 1 + n\beta \cos \phi, \dots (5)$$

the remaining terms being of higher orders in β . Inserting the value of n from (4) we have

$$r_a^n = 1 + \frac{\beta c t s}{2v} \cos^2 \phi \sin \phi d\phi;$$

and since $\beta c t s$ is the infinitesimal increase of volume, Δv , which occurs within the time t as a result of the motion M , this last equation may be written in the form

$$r_a^n = 1 + \frac{1}{2} \frac{\Delta v}{v} \cos^2 \phi \sin \phi d\phi. \dots (6)$$

So far we have considered only the directions between ϕ and $\phi + d\phi$, but meanwhile the given element of energy has also been arriving a large number of times at every other possible angle between 0 and $\pi/2$, and equation (6), with the appropriate value of ϕ , is applicable to every such angle. The total effect of all the arrivals at all possible angles will therefore be to change the period in the ratio given by the product of all the expressions of the form (6) for all values of ϕ ; and dropping terms of higher order in β , the value of this product will be

$$1 + \frac{1}{2} \frac{\Delta v}{v} \int_0^{\pi/2} \cos^2 \phi \sin \phi d\phi = 1 + \frac{1}{6} \frac{\Delta v}{v} \dots (7)$$

If we go on to treat the effects of the departures, the reasoning will be found to be the same all the way through, with the mere substitution of ψ for ϕ , and the total effect will be found, as before, to be to increase the period in the ratio $1 + \frac{1}{6} \frac{\Delta v}{v}$. Hence the combined result of the two sets

of effects, which have in reality been occurring alternately, is to increase the period of every element of the radiation in the ratio

$$\frac{T + \Delta T}{T} = \left(1 + \frac{1}{6} \frac{\Delta v}{v}\right)^2 = 1 + \frac{1}{3} \frac{\Delta v}{v} \dots (8)$$

Replacing the period by the wave-length we therefore have

$$\frac{\Delta \lambda}{\lambda} = \frac{1}{3} \frac{\Delta v}{v} \dots (9)$$

Since this result is independent of the original value of the wave-length λ , it is valid for any value. Hence $\lambda + d\lambda$ and therefore $d\lambda$, the interval within which the wave-lengths are included, is changed in the same ratio as λ .

The result is also valid for any element of the surface of the shell which is small enough to be treated as plane, and for motion either in or out, so that equation (9) may be integrated into the form

$$\lambda = \text{const.} \times \sqrt[3]{v}. \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The meaning of equation (10), reduced to its simplest terms, is as follows:—If the shell changes its volume while retaining its shape, the dimensions of the waves change in the same ratio as those of the shell. The whole system of waves and shell remains geometrically similar to itself, the number of waves present being unchanged.

5. In the foregoing reasoning we have treated the radiation as perfectly diffuse, for the cancellation of $R_\lambda d\lambda$ from the numerator and denominator of equation (4); and the corresponding equation for the case of departure, involved the assumption that R_λ was the same at all points and in all directions. This assumption is not exact, for upon reflexion from a moving mirror the angle of departure ψ' differs from the angle ψ at which the ray would leave a fixed mirror by a quantity of the order of magnitude of the ratio of the velocity of the mirror to the velocity of light. The result of this is that at any point within our shell the radiant vector in directions away from the moving piece M has not exactly the mean value R_λ , but a value

$$R_{\lambda'} = R_\lambda(1 + \epsilon),$$

where ϵ is an infinitesimal of the same order as β . This departure from perfect diffuseness is not cumulative, but remains of the same order of magnitude whatever the lapse of time, for the disturbing effect of reflexion from M is continually being damped out by the diffusing effect of the irregular reflexions from the stationary walls.

If we now review our reasoning, we find that R_λ appears only in the expressions for the total energy within the shell and for the total energy which strikes or leaves M at a given angle within the time t . If R_λ represents the average value which satisfies the equation

$$\int \rho_\lambda d\lambda \cdot dv = 4\pi \frac{R_\lambda d\lambda}{c} \cdot v,$$

the numerator of equation (4) ought to contain not R_λ but $R_\lambda(1+\eta)$, where η is an infinitesimal of the order βq , q being the ratio of the area s to the whole area of the shell walls. The error in n caused by the omission of this factor $(1+\eta)$ is infinitesimal and negligible. The changes caused in equations (5) to (10) by using the exact value instead of the mean value of R_λ would all be of a lower order of magnitude than the terms which have been retained. Hence the error incurred by our treating the radiation as completely diffuse is infinitesimal, and the result expressed in equations (9) and (10) remains valid.

One further point may be worth notice. If "the long time t " appears to the reader to be possibly not long enough to give all the finite amount of energy within the shell an equal opportunity of being reflected from M in every one of the infinite number of conceivable ways, there is no objection to his making it longer, in other words, infinite. If this is done we may still make Δv or $ct\beta s$ infinitesimal, as we want it to be, making βs of the order t^{-2} ; and this may be accomplished either by making

$$\beta = \text{const.} \times t^{-2}$$

with s finite, or by making both β and s of the order t^{-1} . There is nothing to prevent our adopting either course. The use of the more concrete expression a "long" time instead of an "infinite" time did not, therefore, involve an error in the reasoning, while it obviated the necessity of interrupting the argument at an inconvenient point.

6. We have next to consider the change of the energy of the radiation which accompanies its change of period, and we assume that diffuse radiation exerts a pressure equal to one-third of its density on the walls of a containing envelope. This proposition may be deduced in several ways from Maxwell's theory of the electromagnetic field, which has been confirmed in so many respects that we need not regard it as doubtful, but accept its consequences without further discussion.

During an expansion Δv , the work given out is then expressed by $\frac{1}{3}\rho_\lambda d\lambda \cdot \Delta v$; and since the expansion of radiation within a perfect reflector is adiabatic, this work is equal to the simultaneous decrease of the energy within the shell, and we have

$$\frac{1}{3}\rho_\lambda d\lambda \Delta v = -\Delta(\rho_\lambda d\lambda v),$$

whence upon developing, rearranging, and dividing by $\rho_\lambda d\lambda v$ we have

$$\frac{4}{3} \frac{\Delta v}{v} + \frac{\Delta d\lambda}{d\lambda} + \frac{\Delta \rho_\lambda}{\rho_\lambda} = 0.$$

But since $d\lambda$ changes in the same ratio as λ ,

$$\frac{\Delta d\lambda}{d\lambda} = \frac{\Delta \lambda}{\lambda};$$

and if we eliminate v by equation (9) we have

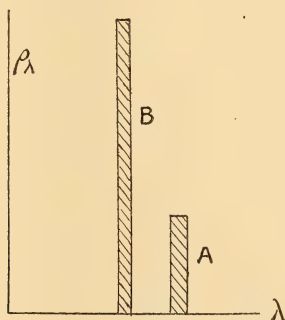
$$5 \frac{\Delta \lambda}{\lambda} + \frac{\Delta \rho_\lambda}{\rho_\lambda} = 0, \quad . \quad . \quad . \quad . \quad . \quad (11)$$

or

$$\rho_\lambda \lambda^5 = \text{const.} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

The meaning of this result is that if approximately monochromatic diffuse radiation of strength $R_\lambda d\lambda$ and density $\rho_\lambda d\lambda$ is compressed or expanded adiabatically and infinitely slowly, the quantity ρ_λ changes as the inverse 5th power of the wave-length, λ itself being subject to equation (10). If the strip A (fig. 1), of width $d\lambda$ and height ρ_λ , represents

Fig. 1.



the original energy density, the strip B, which represents the energy density after compression, has its height increased in the ratio of the 5th power of the ratio of decrease of the width or of mean wave-length. Its area is therefore proportional to the inverse 4th power of the wave-length.

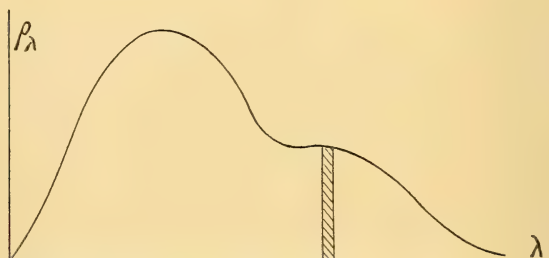
This change of density and the accompanying change of $R_\lambda d\lambda$ do not interfere with the validity of the reasoning by which we found the value of n in equation (4). For since the motion is infinitely slow, the values of $R_\lambda d\lambda$ which have been cancelled from the numerator and denominator may be

treated as always equal, within an infinitesimal amount, in spite of the fact that they are not constant in time.

The width $d\lambda$ may be as small as we please, so that the change of ρ_λ may be assigned definitely to the particular wave-length λ . There is no occasion for the formation of any new waves; the change in energy is a change in the amplitude of waves already present, which occurs in connexion with the change of period upon reflexion from the moving surface. In a *short* time, reflexion from the moving mirror would introduce inhomogeneity into the radiation, which would not have time to be all equally affected by reflexion at M; but in a long time the radiation again becomes homogeneous to the same degree as at first, and equation (12) is satisfied for each wave-length.

7. Hitherto we have considered only a small interval of wave-lengths, but suppose that the strip in question is merely a part of a continuous distribution of diffuse radiation which may be represented by a curve such as is shown in figure 2. If we take full advantage of the principle of the

Fig. 2.



independence of the separate elements composing the whole spectrum, we must admit that the reasoning given above for an isolated strip is applicable without change to every wave-length of the spectrum, no matter what may be the form of the energy curve $\rho_\lambda = f(\lambda)$. We then have the proposition that when any completely diffuse radiation is compressed infinitely slowly within a perfectly reflecting enclosure, the energy curve is changed in such a way that the abscissa of every point is multiplied by some fraction f , while the ordinate is multiplied by f^{-5} , so that the area under the curve, or the integral density of the energy present, is multiplied by f^{-4} . This is true for any continuous or discontinuous spectral distribution and not merely for black radiation.

8. The remainder of the deduction contains nothing new, but may be given for the sake of completeness. Let the shell be filled with black radiation of temperature θ and density ρ , by first covering a hole in the shell with an ordinary body of temperature θ , and then, after equilibrium has been established, closing the hole with a cover which has the same reflecting properties as the rest of the shell wall. Let the volume of the shell, which may, if we prefer, have the form of a cylinder closed by a piston, be decreased a finite amount by an infinitely slow compression. The fact that this requires an infinite time need not concern us. The density of the energy is increased on account both of the work done and of the decrease of volume of the energy already present. The spectral distribution also changes in the manner already given.

At the end of the compression we introduce into the shell a particle of ordinary matter so small as to be of negligible thermal capacity. If the spectral distribution after compression was not that of black radiation of the same integral density, absorption and re-emission by the particle cause a re-distribution and a "blackening" of the radiation without change of density. This establishment of stable equilibrium by re-distribution of the energy among the different periods is spontaneous and therefore irreversible.

We now expand to the original volume. The radiation remains black on account of the presence of the particle, and the work given out is the same as that put in during the compression, because the pressure depends only on the total density of the energy present and not on its spectral distribution. At the end of the cycle, which may be completed by removing the particle, we have therefore re-established the original state exactly. No heat has been added to or taken from any outside body, the work done has been regained, and no changes remain. The cycle is therefore reversible and cannot have included any irreversible element. Hence the introduction of the particle after compression did not cause any change in the spectral distribution of the energy, which must therefore already have been that of radiation from a black body. Hence we conclude that during infinitely slow adiabatic change of density, radiation which was initially black remains black.

9. We may now apply equation (12) to an adiabatic change of the volume and density of black radiation. The integral density changes from that needed for equilibrium with an absorbing shell at the absolute temperature θ_1 to that needed

for some other temperature, θ_2 . The abscissa λ_1 of any point on the original energy-curve is changed to a new value λ_2 , such that

$$\frac{\lambda_2}{\lambda_1} = \chi = \sqrt[3]{\frac{v_2}{v_1}}. \quad \dots \quad (13)$$

At the same time the ordinate of the point changes so that

$$\frac{(\rho_\lambda)_2}{(\rho_\lambda)_1} = \frac{1}{\chi^5}, \quad \dots \quad (14)$$

and the area under the curve, which represents the integral density ρ , changes so that

$$\frac{\rho_2}{\rho_1} = \frac{1}{\chi^4}. \quad \dots \quad (15)$$

But we know by the Stefan-Boltzmann law * that for diffuse black radiation at θ_1 and θ_2

$$\frac{\rho_2}{\rho_1} = \left(\frac{\theta_2}{\theta_1}\right)^4, \quad \dots \quad (16)$$

whence it follows that

$$\chi = \frac{\theta_1}{\theta_2}. \quad \dots \quad (17)$$

From equations (13) and (17) we thus obtain the relation

$$\lambda_1 \theta_1 = \lambda_2 \theta_2, \quad \dots \quad (18)$$

and the displacement law contained in equations (12) and (18) may be stated as follows:—Given the spectral energy curve of black radiation at any temperature θ_1 , to construct the curve for any other temperature θ_2 , multiply the abscissa of each point by $\frac{\theta_1}{\theta_2}$ and the ordinate by $\left(\frac{\theta_2}{\theta_1}\right)^5$. “Corresponding” points on the two curves have the same value of $\lambda\theta$.

From this we may easily deduce the more familiar special forms of the displacement law

$$\lambda_{\max.} \theta = \text{const.},$$

$$\rho_{\max.} \lambda_{\max.}^5 = \text{const.},$$

and

$$\rho_{\max.} = \text{const.} \times \theta^5,$$

* The deduction of this law from the value of the radiation pressure $p = \rho/3$, by using the principle of section 8, is so simple that it may be omitted here.

as well as the fact that if the displacement and Stefan-Boltzmann laws are to be satisfied, the complete equation must have the general form

$$\rho_{\lambda, \theta} = C\lambda^{-5} F(\lambda \cdot \theta).$$

The only novelties in the above deduction, if there are any at all, occur in sections 4 to 7; but it seems to me that greater clearness has been attained without any real sacrifice of rigour, and by only the most elementary means,

Bureau of Standards,
Washington, Feb. 28th, 1912.

XCII. On Transverse Vibrations of a String Maintained by Forces of Double Frequency. By JOSEPH H. T. ROBERTS, M.Sc., University of Liverpool.*

THERE is a type of maintained vibration, which has the peculiarities that the frequency of the imposed variations is twice that of the maintained variations, and that the imposed periodic variations do not tend directly to displace the body from its equilibrium configuration. The most familiar example of such motion is that form of Melde's experiment in which the prongs of the fork vibrate in the direction of the length of the string; the motion of the fork causes the tension of the string to be periodically variable, and there does not appear, at first sight, to be anything to cause the string to depart from its equilibrium condition of straightness; as is well known, however, the equilibrium may become unstable under these circumstances, and the string may be maintained in permanent vibration whose frequency is half that of the fork.

Melde's experiment was one of the methods used by students in this laboratory to determine the frequency of a tuning-fork from the equation

$$l = \frac{1}{n} \sqrt{\frac{mg}{\rho}},$$

but it was found that there was a very considerable range of tension for which a given string would vibrate with a given fork. In this experiment the string was attached to the upper extremity of the prong, and the fork was caused to vibrate by bowing. It was thought that the discrepancy might be due simply to the large motion of the point of

* Communicated by the Author.

attachment of the string. The results obtained by different observers were so widely different as to render the method useless, in its simple form, for the determination of the frequency of a fork.

The theory of these experiments has been given by Lord Rayleigh*, who discusses the modification to which the adjustment of pitch must be subject in practice, in order that the experiment may succeed.

According to the usual theory, the maintenance will be most vigorous when the period of the string, as calculated from its length, tension, and linear density, is exactly twice that of the fork, and this period is calculated for small vibrations. This is not so, however, for, calling the length obtained from the formula the theoretical length, the amplitude of the string increases as the length is made greater than the theoretical length, and the string is still able to begin from infinitely small vibrations. If the string is maintained with small amplitudes, its length is much less than the theoretical length. The period of the string appears to accommodate itself, not only by alteration of amplitude, but also by alteration of plane; it seems not improbable that on account of gravity the period of vibration in a vertical plane will be different from that in a horizontal plane: this view is supported by the fact that frequently the string will choose either of two planes at equal angles on opposite sides of the vertical. It is difficult to study the problem with the simple apparatus referred to above: in order to find out whether the frequency of a fork could really be determined from a knowledge of the period of a maintained string, and to investigate this example of maintenance by a force of double frequency, the following experiments were undertaken.

The apparatus consists of a massive fork about 36 cm. long, supported vertically and placed so that the vibrations take place in the direction of the length of the string; the fork is maintained electrically, the electromagnet being inserted between the prongs at their upper ends, and the string is attached at a point 7 cm. from the shoulder of the fork: in this way considerable driving force is obtained, and the actual motion at the end of the string is extremely small (0.22 mm.). The string consists of a plaited flax cord, of mass .01347 grm. per cm., pulled by a weight suspended over a pulley. In order to make the length of string definite, two stops consisting of straight-edges with V-shaped notches

* Phil. Mag. 1883; 'Sound,' vol. i. ch. 3.

are placed horizontally below the string ; one of the stops is attached to a travelling-microscope table, in order that it may be moved uniformly. The fork is placed on a separate table to prevent direct communication of vibrations.

If a stroboscopic disk, driven in unison with the fork, be arranged so that the eye looks through slits which are moving along the length of the string, then, on account of phase differences, the string appears to have a series of loops (since its frequency is half that of the fork), the number of loops increasing as the eye is withdrawn further from the disk : if the slits move at right angles to the string, a series of straight lines are seen. By examining the string through the disk in this manner, and observing the stability of nodes, a knowledge of the condition of the string can be obtained, and the presence of overtones &c. detected. The amplitude of the fork at the point of attachment of the string was measured in the microscope and found to be 0.22 mm.

The following observations relate to the string vibrating in one segment ; the present note does not include any reference to the results with two or more segments.

If the stops consist simply of horizontal straight edges, the vibrations of the string are executed always in the vertical plane, this being due to the fact that the stops, if smooth, exert no reactions for horizontal vibrations. With the string resting in the notches, however, the plane of vibration is definite, and depends simply upon the length, whether a given length be approached by shortening or by lengthening the string. If the plane of vibrations be displaced from this plane of equilibrium, it returns to it with more or less eagerness, depending upon the length of the string.

The explanation of the mode of action of the string given by Tyndall *, though incorrectly illustrated in his diagram, is well illustrated in the string, every point of which is found to be describing a curve convex towards the fork ; the curvature for points near the fork is greater than for points distant from the fork ; this curvature is, of course, more marked the greater the amplitude of the fork at the point of attachment of the string.

Starting with the length too short for any vibrations to be produced in the string, if the length be gradually increased there will be found a sharply defined point, at which vibrations of very small amplitude will commence ; the plane of these vibrations is usually inclined to the vertical.

* 'Sound,' 2nd ed. p. 105.

As the length is increased the amplitude becomes greater, and the plane of vibrations may change gradually. At a certain point, which, however, is not so well defined as the point where small vibrations begin, the plane slowly rotates to the vertical; for lengths greater than this the plane shows greater and greater preference for the vertical, and the amplitude goes on increasing. At a further point the string is no longer able to start vibrating from its equilibrium condition of straightness, but if it be given a certain initial amplitude, this will immediately develop into a large amplitude. If the length be still further increased there comes a time when the fork is unable to support the large amplitudes with which the string vibrates; the vibrations of the fork are damped down, the amplitude of the string falls in consequence, until it is below the critical value necessary for starting, the string then falls immediately to the straight position, and the fork goes on vibrating vigorously once more. An idea of the lengths at which these effects happen is given by the following table.

TABLE I.

Normal tension = 500 grams weight.

Mass per unit length of string = 0.01347 grm. per cm.

Amp. of fork at point of attachment of string = 0.22 mm.

Frequency of Fork.	Calculated length (cm.).	Least length at which very small vibrations begin (cm.).	Greatest length at which very small vibrations can begin (cm.).
32.0	188.7	181.3	195.9
40.0	150.9	141.7	156.7
42.85	140.8	137.1	146.6
49.18	122.7	119.4	127.0

It will be seen that the frequency of the fork, if unknown, could not be calculated from any of the numbers given in Table I. It was observed, however, that the length when the plane of vibrations began to show a preference for the vertical was always about the theoretical length, and this appears to be the only length which bears any easily recognized relation to the theoretical length. Some numbers illustrating the coincidence of these lengths are given in Table II.

TABLE II.

Conditions as in Table I.

Frequency of Fork.	Length (cm.) when plane becomes vertical.	Calculated length (cm.).
32.15	189.4	187.7
39.34	153.9	153.3
40.0	151.0	150.9
42.85	141.0	140.8
44.72	136.3	134.9
49.18	122.1	122.7
52.94	114.0	114.0

It might be expected that the theoretical length would occur with very small amplitudes; at present this does not appear to be the case, but it must be remembered that although the amplitude of the fork at the point of attachment of the string is so small (0.22 mm.) it may, nevertheless, be too great for the theoretical conditions to be realized. It is not surprising that the maintenance at the theoretical length is not the most vigorous, for the theory shows that a large amplitude may be necessary for the requisite accommodation of pitch. It is remarkable that with the large amplitudes of the string the reaction upon the fork should be sufficient to damp down its vibrations so much, considering the powerful electrical maintenance; it is no doubt due to an adjustment of phase difference. It is to be noticed that the mode of action of the string is not precisely the same when under free vibration and when under maintenance of the kind considered; for in the former case the condition of the string is symmetrical about the mid-point, while in the latter case every point of the string describes a curve convex to the fork; in the former case also the tension is greatest at the furthest point of a swing, in the latter it is not. In some cases the pulley was observed to be rotating slowly.

In order to find out whether a vibration were merely maintained with an adjustment of amplitude for the requisite accommodation of pitch, the string was supported in the same manner as before, except that it was attached to a support and detached from the fork; the stroboscopic disk

was driven in unison with the fork, and the string was given a small free vibration of the same amplitude as that which had been maintained by the fork. On examining this through the disk, it was found to be giving perceptible beats with the fork. Thus a string with the same amplitude could vibrate with two different frequencies: it seems that the vibration of the string is not merely a maintained vibration with an accommodated pitch, but is to some extent a forced vibration. At the theoretical length the free vibration gave no beats when examined through the disk. Experiments upon this point are still in progress.

Conclusion.

The range of length over which a string can be maintained in vibration by a given fork is so great as to render the ordinary form of Melde's longitudinal experiment useless for the determination of the frequency of a fork. The period of vibration of a string can accommodate itself by adjustment of plane as well as by adjustment of amplitude. The length of the string when vibrations of very small amplitude just begin is considerably less than the theoretical length. When the theoretical length is reached the plane of vibrations becomes vertical, and this provides a means of making the experiment definite; with horizontal straight-edge stops the plane is always vertical. When the length is greater than the theoretical length, the amplitude increases until, at a certain length, vibrations are only possible when they exceed a certain critical initial amplitude; this critical amplitude increases with further increase of length. At a still greater length the reaction upon the fork is very considerable indeed. By stroboscopic examination, a string is found to have different periods, for the same amplitude, when free and when maintained; its maintained vibration must be to some extent a forced vibration.

The discrepancy between theory and practice was observed by Professor Wilberforce, who thereupon suggested the investigation, and I desire to thank him for the interest which he has shown in the experiments.

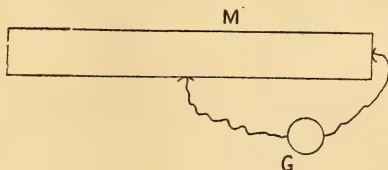
George Holt Physics Laboratory,
University of Liverpool.

XCIH. *Unipolar Induction.* By E. H. KENNARD*.

ONE of the chief characteristics of Lorentz's Electron Theory is the assumption that electromagnetic phenomena depend in part on motion through an æther which is everywhere at rest, but this principle has not yet been tested by any method which employs only quasi-stationary phenomena. It is, however, involved in a simple manner in unipolar induction, and this would seem to render a definite solution of that much-debated problem very desirable.

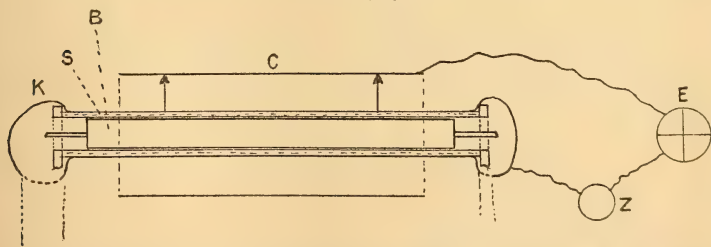
In the classical form of unipolar induction discovered by Faraday, a bar-magnet (M) (fig. 1) is rotated about its axis of magnetic symmetry, while a wire leading to a galvanometer

FIG. 1.



(G) makes sliding contact with it at one end and in the middle. In the circuit so formed an E.M.F. is developed whose amount is always given by Faraday's law of induction. Two views as to the seat of this E.M.F. have been held: (1) that it is produced in the wire, which is at rest, as the magnetic force lines rotating with the magnet cut through it; (2) that it is produced in the magnet itself as the latter moves through its own magnetic field. It is clearly impossible to decide between these two views by any observations on closed circuits; hence, in the present investigation an electrometer and an open circuit were employed.

FIG. 2.



The apparatus is shown diagrammatically in fig. 2. A steel bar (B), 2 feet long and 2 inches in diameter, was mounted

* Communicated by Prof. J. S. Townsend, F.R.S.

inside a solenoid (S) by means of which it could be magnetized at will, and the whole supported about 4 feet off the floor. The bar, which will hereafter be referred to as the magnet, was set in rotation by means of a motor. Concentric with the solenoid was placed an insulated metal cylinder (C) shorter in length but of larger diameter. The solenoid and all connected parts, including the motor and belt, were surrounded with a continuous metal case (K), which was put to earth and served to protect the outer cylinder from electrostatic disturbances originating inside the case. The outer cylinder was connected with a quadrant electrometer (E) placed nearly in line with the axis of the magnet.

The outer cylinder was about 49 cm. long and 20 cm. in diameter. The case surrounding the solenoid, which will be referred to as the "inner cylinder," was 7.3 cm. in diameter. The electrometer scale gave very nearly 850 divisions per volt.

In this apparatus either the inner cylinder, which was earthed (Z) and therefore communicated with the end of the magnet through the axle, or the outer cylinder and the wire leading from it to the electrometer and so to earth (when the electrometer was earthed) and back to the end of the magnet, might be regarded as corresponding to the wire in Faraday's experiment, only the sliding contact at the centre and a short connecting wire being omitted. Hence, if in Faraday's experiment the E.M.F. was produced in the wire, it will here be produced in the cylinders and connecting wires; these will then come to some electrostatic potential different from that of the earth and the outer cylinder will be charged. If, on the other hand, the E.M.F. is produced in the magnet, it could influence the outer cylinder only through electrostatic induction, and such effects are screened off by the earthed metal case. Thus, by observing the effect on the electrometer, it is possible to determine the seat of the E.M.F.

The first view corresponds to what may be called the "Moving Force Line Theory." According to this theory the electromotive intensity E' at any point in the circuit is given by

$$E' = E + \frac{1}{c} [V'H],$$

where E is the electric force and $[V'H]$ is the vector product of V' , the velocity of the circuit "relative to the magnetic force-lines," *i. e.*, to axes fixed in the magnet, and H is the magnetic force. This theory secures *complete* relativity, that is, the phenomena depend only on the relative translation *or*

rotation of the material bodies concerned, a principle which has often been assumed almost as an axiom in treating of electromagnetic phenomena.

In the steady state E' must vanish everywhere, hence

$$E = -\frac{1}{c} [V'H].$$

From this it is easily shown by integration that if ϕ is the electrostatic potential at any point on the cylinders, the potential at infinity being taken as zero, then

$$\phi = \frac{\omega'N}{2\pi c}, \dots \dots \dots (1)$$

where ω' is the angular velocity of the cylinders relative to the magnet, and N is the total magnetic induction through the periphery of the cylinder at the point in question.

It is worth noting that, according to this theory, the vector E' in general fails to satisfy Laplace's Equation, even where there is no volume distribution of electricity. If this were not true, all effects due to electromagnetic induction would, of course, be screened off by the metal case enclosing the solenoid and magnet.

The second view is taken by Lorentz, who puts

$$E' = E + \frac{1}{c} [VB],$$

where V is the velocity relative to the æther and B is the magnetic induction. Hence in the steady state

$$\phi = \frac{\omega N}{2\pi c}, \dots \dots \dots (2)$$

where ω is the angular velocity of the cylinders relative to the æther. We see that if the magnet were at rest while the cylinders rotated, then (1) and (2) would be identical and the two theories lead to the same results; if, however, the cylinders are at rest and the magnet rotates, as was the case in the present experiment, then, according to (2), ϕ vanishes, while according to (1) it is the same as before, so that in this case the two theories lead to opposite conclusions.

Evidently N and ϕ will be practically the same for both cylinders, so that the charges on the inner surface of the outer cylinder, and on the outer surface of that portion of the inner cylinder which is enclosed by the outer, will be small; most of the electrification required by the Moving Force Line Theory will be on the outer surface of the outer

cylinder. Now while the magnet is rotating let the electrometer be disconnected from earth and let the magnetization be then reversed. N and ϕ then change sign, so that part of the electrification on the outer cylinder will be driven on to the electrometer and a deflexion will result.

In practice the electrometer was left insulated while the position of the spot was read every 60 seconds and the direction of magnetization reversed immediately after each reading. By rotating the magnet first in one direction and then in the other, which changes the sign of the effect due to electromagnetic induction, and then combining the deflexions obtained in the usual manner, the effect of disturbances was largely eliminated from the final result.

The only results obtained with the apparatus entirely in its final form consist of 3 series aggregating 70 observations. The greatest deflexion during any period of 60 seconds was ± 11 divisions of the scale, while the mean numerical deflexion was less than 4 divisions for each series. For the effect apparently due to electromagnetic induction when the magnetization was reversed, these observations yield the values $+0.65 \pm 0.34$ (probable error) and -0.7 ± 0.35 ; mean, 0.0 ± 0.24 . The value zero is thus a very probable value for the true deflexion.

This conclusion is supported by all the inferior series of observations, which show much larger irregular disturbances. That this negative result was not due to defective insulation is evident from the fact that the spot always drifted slowly across the scale when the electrometer was not earthed; in addition, the insulation was always carefully tested at the start, and on several occasions artificial deflexions were produced while the magnet was in rotation, either by altering the electrostatic potential of the inner cylinder or by charging up the outer cylinder and then connecting it to the electrometer.

In order to determine the magnitude of the effect to be expected according to the Moving Force Line Theory, N was determined with a ballistic galvanometer at various points on both cylinders. Its maximum value was found to be 350,000 C.G.S. units. The speed was about 72 turns per second, so that the maximum value of ϕ would be ± 0.25 volt; on the outer cylinder ϕ was about $1/10$ less than on the inner.

From these results and from observations on the capacity of the electrometer and connexions a rough calculation of the theoretical deflexion was made. Corrections are necessary on account of the charge bound inside the outer

surface of the inner cylinder by the radial component of $\frac{1}{c} [V'H]$, which diminishes the result by about 5 per cent., and for the effect of floor and ceiling, which might further diminish it by as much as 10 per cent. The value thus obtained for the total charge on the outer cylinder when earthed was 0.008 electrostatic C.G.S. unit, and for the deflexion on reversal of the magnetization, 41.0 divisions.

In order to check this very rough calculation, the metal case around the solenoid was divided into several insulated sections, and both it and the outer cylinder were charged by means of a potentiometer to known potentials; by connecting the outer cylinder to the electrometer (previously earthed), deflexions were obtained in imitation of the main experiment, some of them while the magnet was in rotation. From these observations and the corrections described above, the theoretical value of the deflexion was found to be 36.0 divisions.

From these two values it was decided, after considering the degree of accuracy of each observation and approximation in turn, that the deflexion required by the Moving Force Line Theory was probably about 37.0 divisions, pretty certainly greater than 31.0, and could not have been less than 26.0 divisions.

The Moving Force Line Theory is thus disproved. In future, whenever the electromotive intensity due to electromagnetic induction is assumed to be proportional to motion relative to magnetic force lines, these force lines must be supposed to be always stationary, at least as regards any rotation of the magnetic system about an axis of magnetic symmetry. That is, a rotating magnet does not "carry its force lines" around with it.

It is thus rendered probable that electromagnetic induction caused by motion depends on absolute motion—that is, on motion relative to the æther, not on motion relative to material bodies. The result thus tends to support Lorentz's theory; but the method is not capable of distinguishing, for instance, between the theories of Lorentz and of Hertz, so that it leads only to a partial solution of the problem. It is the author's hope that a further investigation by another method, which is now under way, will lead to a complete solution.

In conclusion, I wish to express my gratitude to Prof. J. S. Townsend, for his assistance and advice, without which the experiment could never have become an actuality.

XCIV. *The Rectification of the Spectrum in Relation to the Shift of Ellipses in Displacement Interferometry.* By C. BARUS, Ph.D., LL.D., Hazard Professor of Physics, Brown University, Providence, R.I., U.S.A.*

1. *Introductory.*—In my work of last year † the quantity $\mu - \lambda \frac{d\mu}{d\lambda}$ (μ index of refraction of glass, λ wave-length) occurred in the reductions, and in the absence of direct data I temporarily made use of the corresponding quantity computed from standard data for a somewhat similar glass. In this way the amount of displacement of the centres of ellipses per cm. of displacement of the micrometer was determined. It must, however, frequently be necessary to find $d\mu/d\lambda$ from a small piece of glass, and I have therefore tested the following method in which a Kohlrausch total reflectometer slides along the graduated rail of Rowland's adjustment for the grating, as modified for the plate grating by M. Barus and myself ‡.

The method is then further modified, in a way that is applicable when a glass grating is given for investigation, as in the immediate problem, but not otherwise. It admits of some interesting applications, as for instance to the refraction of the material of film gratings.

In all cases of solids, the refraction of the more strongly refracting liquid in which the solid is submerged must of course be known for all wave-lengths; but this is the case for carbon disulphide. If the liquid indices are not known throughout, in terms of wave-length, they may be determined by aid of an air-plate, using virtually the same apparatus and method. I shall give examples of all these measurements below.

2. *Apparatus.*—In fig. 1 AA and BB are the two fixed rails of Rowland's adjustment at right angles to each other, R, joining the vertical axes at a and p , is the cross rail, stretching from the slide D which carries the grating g to the slide C which carries the total reflectometer T. Slides C and D move at right angles to each other, and the position x of C is measured along the brass millimetre-scale SS by aid of the vernier v .

* Communicated by the Author.

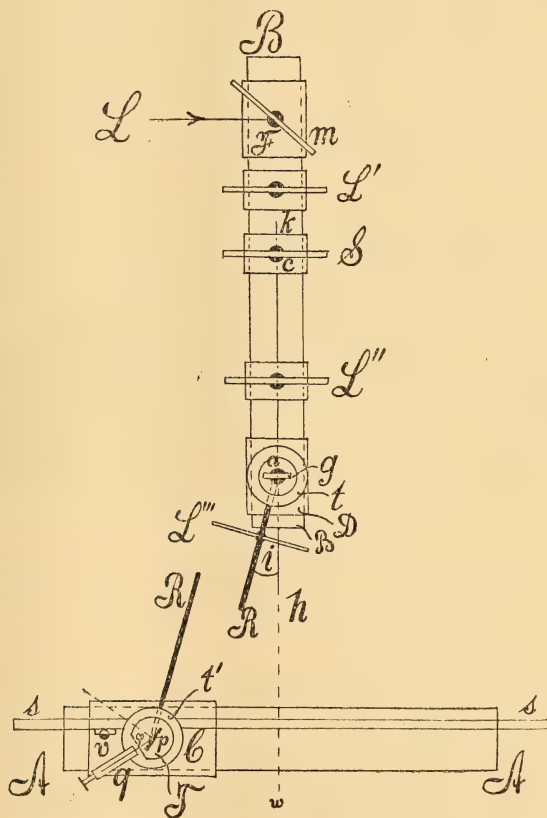
Abridged from the Report to the Carnegie Institution of Washington, U.S.A.

† Carnegie Publications, No. 149, 1911. "The Production of Elliptic Interferences in Relation to Interferometry," Phil. Mag. [6] xxi. p. 411 (1911).

‡ American Journal, xxxi. pp. 85-95 (1911).

The rail BB is further provided with a slide F for the plane mirror *m*, by which white light is thrown upon the slit *c* on the slide S, through the condensing lens *L'*. *L''* is the achromatic collimating objective, and the rod *k* (which may

Fig. 1.



be grasped in front at *h* when necessary) is adapted for clamping *S* and *L'* together, at the principal focal distance of the latter. The collimator *SL''* does not move with *D*. The grating *g*, fixed to a horizontal disk with a spring and three levelling screws, is securely fastened to the table *t*, which here preferably rotates (not shown) with the end *a* of the rod *R*. The grating, in other words, is kept normal to *R*, so that the angle of diffraction is zero, while the angle of incidence alone varies when *C* passes from end to end

of AA. If x_1 and x_2 measured on S be the positions of C for identical lines of the spectrum,

$$\lambda/D = (x_2 - x_1)/2R,$$

where D is the grating space and R the length *ap*.

The lens L''' on R is the objective of a telescope which focusses the coloured image of the slit at the slide C, so that it may there be viewed by an ocular preliminarily. The latter is held in a standard placed on the table t' revolving on a common axis p with this end of R. When the ocular is replaced by the total reflectometer T, of which p is the plate of glass (properly centred) to be examined and q the telescope, the weak lens L''' is superfluous; but as a rule it need not be removed, and is rather advantageous in condensing light when sunlight is not used.

When sunlight is used, the lens L''' may be moved slightly backward, so as to put the coloured images of the slit slightly in front of a cylindrical glass vessel T of the total reflectometer. If the adjustment is properly made the lines are adequately visible in the telescope q , and the index may be found for a given Fraunhofer line without reference to the scale *ss*. Without sunlight, the scale *ss* is essential. Naturally the images seen in the telescope are not sharp, inasmuch as the cylindrical mantle of the bottle acts as one of the lenses; but they are clear enough for the purpose. It is usually more satisfactory, however, to ignore the lines and to determine the index of refraction for successive positions x of the carriage C on the rail AA, given by the scale *ss*.

With the total reflectometer revolvable, as a whole, on its axis, the two symmetrical positions of q relative to R give the double angle of total reflexion, or 2ϕ , for the given liquid (usually carbon disulphide) in which the glass plate p is submerged. The graduated circle of the instrument with which the telescope q is rigidly connected is available for the measurement of angles.

3. *Methods*.—When the air plate is used for the measurements of the indices of refraction of the liquid, the telescope q is directed along the rail R and $2\phi_i$ found by rotating the plate, p , until the two limits or ends of the visible part of the spectrum successively coincide with the cross-hairs. The spectrum is usually nearly homogeneous in colour; but the ends are liable to show interference fringes. Simultaneously the position x of the slide C and the temperature t of the

liquid are read off. Thus if

$$N_t = 1/\sin \phi_t$$

be the index * of the liquid at t° ,

$$N_{20} = N_t(1 + \alpha(t - 20)) = (1 + \alpha(t - 20))/\sin \phi_t$$

is the index at 20° . For carbon disulphide, at mean temperatures, $\alpha = .0008$, nearly.

Again, if the glass plate is now introduced and similar measurements ϕ_t , t' be made at x , the index of the plate will be

$$n = N_t \sin \phi_t' = N_{20} \sin \phi_t' / (1 + \alpha(t' - 20)),$$

or

$$n = \sin \phi_t' (1 + \alpha(t - t')) / \sin \phi_t'.$$

Two symmetrical sets of values are thus obtained, one for *each of the two first orders of spectra*, at x_1 and x_2 , on opposed sides of the undeviated white ray, w . This method does not usually succeed very well; for it presupposes that in case of the air plate and glass plate, which are successively inserted, the total reflexion occurs at identical parts of the spectrum, for identical positions x along the scale s . But supposing the adjustment trustworthy, the wave-length corresponding to any given n is found from the two positions x_1 and x_2 at which the same n occurs, from the equation

$$\lambda = D(x_2 - x_1)/2R.$$

In general it is preferable to use the air plate first to find the indices of refraction of the liquid, if these are not known throughout the spectrum. There will thus be given two symmetrical curves for the two first orders of spectra, separately. Their distance apart $x_2 - x_1$ for the given values of N determines the wave-length, λ , sought; *i. e.*, if N is plotted in terms of x , the horizontal distance apart of the two curves is the $x_2 - x_1$ which determines the wave-length for the index N selected. Hence N is given in terms of λ and should be reduced to 20° . In case of many liquids, in particular carbon disulphide, N is well known in terms of wave-length at the outset, so that the air plate is superfluous.

The observations with the glass plate are made in the same way. The symmetrical curves for $\sin \phi_t'$ at t' , reduced to $\sin \phi'$ at 20° , as found from the two first orders of spectra, are plotted in terms of x . Hence their distance apart for two

* In conformity with Kohlrausch's notation N and n are here used as symbols for index of refraction.

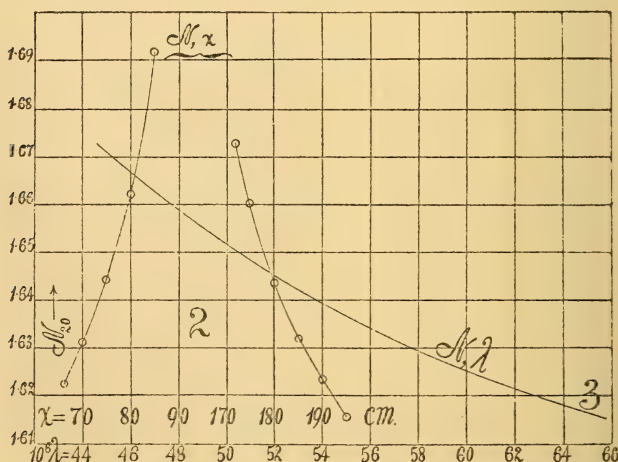
equal values of $\sin \phi'$ is $x_2 - x_1$, from which the wave-length λ is computed. This datum in turn gives the appropriate (known) value N of the index of the liquid, all at 20° , so that finally

$$n = N \sin \phi'.$$

4. *Examples. Liquids.*—The circle of the Kohlrausch total reflectometer is only a little over 3 inches in diameter, and the reading is just within $\cdot 1$ degree of arc. The index of carbon disulphide moreover varies, relatively speaking, in marked degree with temperature; *i. e.*, $\cdot 0008$ per degree C. Unless unusual precautions are taken, therefore, one cannot expect the units of the third place to be quite trustworthy, as it corresponds to about $\cdot 07^\circ$ of arc. The apparatus in my possession was an old instrument, and a high order of precision was of secondary interest, and not attempted.

I will first take the case of an air plate with carbon disulphide. A film of air was enclosed between two small plates of microscope cover-glass by cementing them at their edges with glue. In another case, plates of glass $\cdot 3$ cm. thick were similarly prepared. An example of the results is given in the curves fig. 2, which show the value of N_{20} in terms of x .

Figs. 2 & 3.



These curves should be quite symmetrical to the vertical, so that for any height, N_{20} , $(x_1 + x_2)/2$ is constant.

Similarly a given horizontal N_{20} determines the values $x_2 - x_1$ for the computation of the wave-length λ . The film of

the grating had nominally 15,050 lines to the inch, and the oblique rail R was 169.4 cm. long. Hence

$$\lambda = \frac{x_2 - x_1}{15,050 \times .3937 \times 2 \times 169.4} = 4.98 \times 10^{-7} (x_2 - x_1).$$

These values x_2 , x_1 , λ , and N_{20} are given for the successive values of N_{20} used, and fig. 3, which is therefore the corresponding dispersion curve for carbon disulphide at 20° .

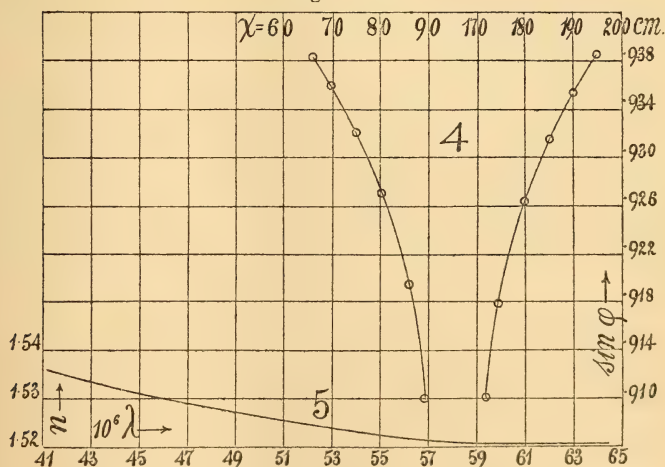
5. *Examples. Solid.*—The treatment of a solid medium is similar, except that the total reflexions are observed by reflected light. If the data for carbon disulphide be taken at 20° ,

$$n = N_{20} (1 - \alpha(t - 20)) \sin \phi.$$

Fig. 4 shows the values of the corrected $\sin \phi$ in terms of x . The curves, as they should be, are nearly symmetrical to the vertical, or $(x_1 + x_2)/2$ is nearly constant for the same sine.

If now the distance apart of equal values of the reduced $\sin \phi$ be taken, *i. e.*, if $x_2 - x_1$ be found for suitable increments of $\sin \phi$, the former values determine λ , from which the corresponding N_{20} for carbon disulphide is found in turn.

Figs. 4 & 5.



In this way the data for the values of n to be computed are found, and n may now be expressed in terms of the λ used. If N_{20} for carbon disulphide be taken from Kohlrausch's tables, fig. 5 shows the final dispersion curves, index of refraction n varying with wave-length λ , for the glass of the

grating. The constants of these curves will be computed below and their character will then appear.

6. *Independent Measurements.*—As an example of coordinated work, in which the index of the liquid and of the solid are simultaneously found, the following experiment may be cited. The air plate was enclosed between two thin plates of microscope cover-glass. In such a case the limits of total reflexion are determinable both for the reflected rays and for the transmitted rays. The angle ϕ in the former case gives the index of refraction n of the glass in relation to the liquid (carbon disulphide) since

$$n = N \sin \phi;$$

whereas the angle ϕ_0 in the latter case gives the index of the liquid alone, or

$$N = 1/\sin \phi_0.$$

Hence

$$n = \sin \phi / \sin \phi_0,$$

needing no correction for temperature.

In an experiment made at $18^\circ.3$ with the plate of microscope glass in question enclosing the air film, $\phi = 68^\circ.90$ and $\phi_0 = 38^\circ.02$, whence $n = 1.5198$. Using $\phi = 68^\circ.90$ as found and the tabulated data for carbon disulphide from Kohlrausch, $N = 1.6291$, $n = 1.5199$, which happens to agree accurately with the preceding n .

7. *Prism (Liquid CS₂) and Submerged Grating.*—The present method for the above purpose makes use of the grating directly. This is enclosed in a suitable closed trough, preferably triangular in form, with windows of plate glass and filled with carbon disulphide. If the grating is mounted with its ruled face coinciding with the axis of rotation, as in Kohlrausch's total reflectometer, the angle of total reflexion may be measured in all parts of the spectrum. The Fraunhofer lines which are simultaneously in focus are used for reference in succession. Parallel rays of sunlight from a collimator are thrown into one face of the liquid prism, nearly normally to its plane. They emerge at the other face. The undeviated rays are ignored, while the telescope is directed toward the first order of diffraction spectra, this emergence also, for the given grating, being not far from normal. Like the first order of spectra, the second and third orders may often be used with advantage, the limit of total reflexion being identical in all spectra on the same side of the undeviated ray.

The limit of total reflexion moves through the spectrum both with the rotation of the prism as a whole (which must

therefore be on an axle), and with the independent rotation of the grating actuated by the alidade. In the definite adjustment this limit must coincide both with the spectrum line λ for which the index, n , is to be found, and with the cross-hairs of the telescope. Three lines, in other words, are to be brought into coincidence; but after a little practice this succeeds fairly well, unless the limit of total reflexion is too faint.

The difference in angular reading on the two sides of the undeviated ray is the double angle of total reflexion, 2ϕ . The adjustment in the first spectrum holds equally for the second and third orders; and it is in the latter that the phenomenon is liable to be particularly clear and the adjustment correspondingly precise. The beam of white light should illuminate the whole grating whose ruled face is very nearly on the axis of rotation of the alidade. Sunlight is essential for these measurements, since the spectrum lines are to be used. This was not of course necessary in the preceding paragraph.

The following example of results obtained in this way may be given

Line.	2ϕ .	t .	n .	n from figs. 5 &c.
D	$138^{\circ}28$	$19^{\circ}0$	1.5210	$\begin{cases} 1.5215 \\ 1.5206 \end{cases}$
E	$136^{\circ}53$	$18^{\circ}7$	1.5244	$\begin{cases} 1.5240 \\ 1.5250 \end{cases}$

which is practical coincidence within the errors of observation, and thus verifies the above work as a whole.

8. *The Dispersion Constants of the Glass of the Grating.*—To reduce these data for practical purposes it will be sufficient within the range and relatively to the precision of observations to assume the simplified form of Cauchy's equation,

$$n = A + B/\lambda^2,$$

if n_E is the index for the E line and λ_E its wave-length,

$$n - n_E = B \left(\frac{1}{\lambda^2} - \frac{1}{\lambda_E^2} \right),$$

from which B may be computed for each pair of values of n and λ . B was found separately from each of the curves (like fig. 8). The values of $n - n_E$ and λ are chosen as near the observations as possible.

From these results the value of the differential coefficient

$$\frac{d\mu}{d\lambda} = -\frac{2B}{\lambda^3}$$

may also be obtained for any wave-length λ . This and the corresponding value * of

$$\mu - \lambda \frac{d\mu}{d\lambda} = \mu + \frac{2B}{\lambda^2}$$

needed in § 9, in the reduction of the observations of the earlier paper † will be computed by accepting the mean value $B \times 10^{10} = .48$.

9. *Computation of the Shift of Centres in Elliptic Interferometry.*—In the preceding report ‡ I showed that the path difference, y , corresponding to the centres of ellipses throughout the spectrum is

$$y = \frac{e}{\cos R} \left(\mu - \lambda \frac{d\mu}{d\lambda} \right), \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where e is the thickness of the ruled glass plate and μ its index of refraction, for any given colour of wave-length λ . R is the corresponding angle of refraction for light incident at an angle I , or $\sin I = \mu \sin R$.

In the former experiment $I = 45^\circ$. In view of the oblique position of the grating, however, the micrometer motion N of the opaque mirror introduces an additional displacement. Let N be the coordinate for this mirror. Then

$$N = y - e\mu \sin R \tan R. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Hence the readings of the micrometer are determined by (subscripts c referring to centres of ellipses),

$$N_c = \frac{e}{\cos R} \left(\mu \cos^2 R - \lambda \frac{d\mu}{d\lambda} \right). \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Taking the E line as a standard of reference, N_c and the quantities here in question were now computed both for light crown glass ($10^{10}B = .456$, in accordance with the data for μ and λ given in Kohlrausch's tables) and for the glass of the grating actually used ($10^{10}B = .48$), as measured in paragraph 8. Δy_c and ΔN_c refer to distances from the value corresponding to the E line. N_c , y_c , and λ are to be given in centimetres, and the angle of incidence is 45° . The data determine the full lines in fig. 6.

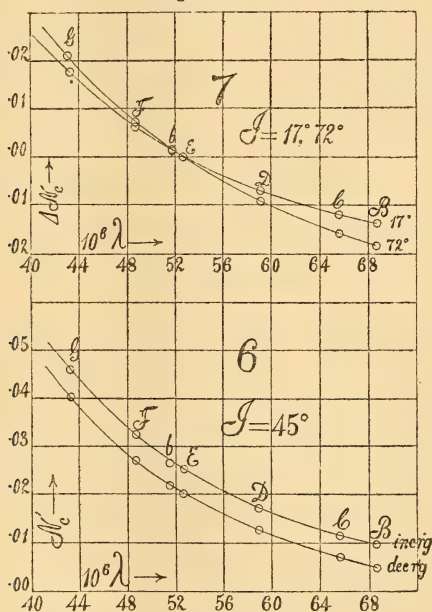
* The symbol μ for index of refraction is resumed.

† Carnegie Publications, No. 149, p. 69 (1911).

‡ Carnegie Publications, No. 149, 44, p. 66 *et seq.* (1911).

Measurements of N_c were now made with the aid of a Fraunhofer micrometer reading to a few ten-thousandths of a centimetre. The opaque mirror was adjustably mounted on a slide and moved normally to itself, in order to put the centres of ellipses successively in coincidence with the B, C, D, &c. lines of the spectrum. At each coincidence a reading was made, care being taken to proceed in one direction only. As there are four spectra more or less in coincidence, it is easily possible to select the wrong line.

Figs. 6 & 7.



By temporarily screening off the reflexion from one mirror, however, and then marking the line desired of the remaining pair by the cross-hairs of the telescope, mistakes are usually avoidable. In the extreme blue and red it was often difficult to see the lines clearly in the superimposed spectra, so that the data for the B and G lines are not quite so trustworthy. In fact the ellipses come out sharpest when but a narrow strip of the grating is used; whereas the resolving power of the grating or general sharpness of lines increases with the breadth of the grating. If the whole grating is used (an intense spot of sunlight focussed on the slit), the adjustment must be very perfect and the surfaces quite true to bring out the ellipses; this is not the case if parallel rays fall on the

slit and the whole divergence in the collimator is due to the diffraction of the slit. With optical plate none of these difficulties would appear.

Apart from drawbacks of this nature, which require patience for their removal, the measurements (shown by little circles in the curves) are quite satisfactory as a whole, as may be seen in fig. 7.

Different values of $(N'_e)_E$ in the two series of fig. 6 are due to the backlash in the micrometer*, as the mirror travelled in opposed directions in these cases. If the observed mean data are compared with the computed data for ΔN_c , the results are practically coincident except at the G line, where the ellipses were too dark to be seen distinctly. Hence equation (3) for N_c may be accepted as correct. If we write it

$$N_c = \frac{e}{\sqrt{\mu^2 - \sin^2 I}} \left((\mu^2 - \sin^2 I) - \mu \lambda \frac{d\mu}{d\lambda} \right), \quad (4)$$

and put $m^2 = \mu^2 - \sin^2 I$, $x = \log \mu$, the equation becomes

$$N_c = e \left(m - \frac{dm}{dx} \right). \quad (5)$$

On integration and reduction this may be written

$$e\mu \cos R = \lambda (C - \int N_c d\lambda / \lambda^2), \quad (6)$$

where C is a constant of integration. Unfortunately equation (6) is too complicated for the computation of μ , when N_c is observed in terms of λ throughout the spectrum; for the reference to the standard E line gives ($\sin I = \text{constant}$)

$$\sqrt{\mu^2 - \sin^2 I} / \lambda - \sqrt{\mu_E^2 - \sin^2 I} / \lambda_E = -\frac{1}{e} \int_E \Delta N_c \frac{d\lambda}{\lambda}. \quad (7)$$

If, however, I is very small, or $R=0$,

$$\frac{\mu}{\lambda} - \frac{\mu_E}{\lambda_E} = \frac{1}{e} \int \Delta N_c \frac{d\lambda}{\lambda}. \quad (8)$$

Let $\mu = B(1/\lambda^2 - 1/\lambda_E^2)$ as above. Then either equation (3) or equation (8) for $I=0$, leads to

$$(\Delta N_c)_0 = (N_c - N_E)_0 = 3eB(1/\lambda^2 - 1/\lambda_E^2). \quad (9)$$

This equation is to be tested in the following paragraph.

10. *Continued. Case of $I=0$.*—The limiting values of I in equation (7) are interesting. They correspond to the form of interferometer approached in fig. 8, where g is the face of

* N' refers to the arbitrary zero on the drum.

the grating, I the incident ray, M and N the two opaque mirrors symmetrically inclined relatively to the grating. Rays R are refracted and rays D are diffracted. In fig. 8

Fig. 8.

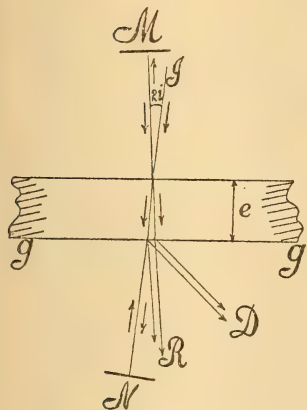
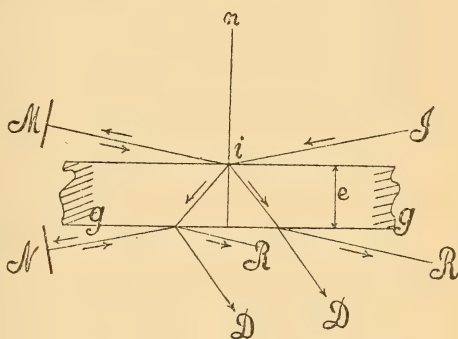


Fig. 9.



the spectra on the left of R are also available ; but they are often complicated with the orders of spectra of the undeviated ray before it has been reflected. To avoid these, one should observe between the spectra of the non-reflected ray, or else in the region of non-reflected spectra of the third or higher orders, as these are too faint to interfere with the reflected spectra. They often advantageously supply fixed lines in the spectrum when arc light is used.

To realize the condition of small angle, a collimator I and the mirror N (micrometer movable parallel to itself) were fixed on the edge of the spectrometer-plate diametrically opposite to each other. The mirror M, the grating *g g*, and telescope at R or D were revolvable around the axis of the spectrometer. Grating and mirrors could be clamped. With such an adjustment all values of *I*, in fact, may be tested between 10° and 80° , smaller and larger angles being excluded, because of the lateral dimensions of the apparatus and mounting.

The present method of interference is often exceedingly convenient, inasmuch as the telescope at R is almost in contact with the micrometer at N, which may therefore be manipulated with ease by the observer. A typical form of instrument now completed will be described elsewhere.

The endeavour may now be made to compute B from the

shift of ellipses as suggested in the preceding equation (9) or

$$\Delta N_c = 3eB(1/\lambda^2 - 1/\lambda_E^2).$$

If we compute β in

$$\Delta N_c = \beta(1/\lambda^2 - 1/\lambda_E^2)$$

from the observed value of ΔN_c , the mean value for the B, C, D, F, G lines is found to be $\beta = .975 \times 10^{-10}$. Since $e = .68$ cm. and $B = .48 \times 10^{-10}$ in table 6, $3eB = 10^{-10} \times .979$, which agrees very nicely with the computed value of β just stated.

The full line in fig. 7 contains the data computed for N_c , in case of $I = 17^\circ$ and the glass of the grating ($B \times 10^{10} = .48$). Fig. 7 (upper curve, marked 17°) distributes the observation on the computed curve for ΔN_c , where ΔN_c for the E line is zero.

11. *Case of $I = 90^\circ$ nearly.*—The further case of interest corresponding to fig. 9, where the angle $I = 72^\circ$, and as large as it could be made in the given spectrometer. The spectra were very fine and sharp, but too dark at the violet end and red end.

The computed graph with the observations located with reference to it, is given in fig. 7 on the curve marked 72° . The two curves together indicate the change of sensitiveness on passing from a very small to a very large angle, the slope of the curve, fig. 6, where $I = 45^\circ$ being intermediate. The method of interference given in fig. 9 is useful when observations are made with polarized light (as in the examination of doubly refracting media) and the observer finds it convenient to be near the polarizer at the slit.

12. *Summary.*—I conclude therefore that the observations made at angles of incidence $I = 45^\circ, 17^\circ, 73^\circ$, have verified the equation

$$N_c = e \cos R \left(\mu - \frac{\lambda}{\cos^2 R} \frac{d\mu}{d\lambda} \right) = e \cos R \left(\mu + \frac{2B}{\lambda^2 \cos^2 R} \right)$$

from the shift of the centres of the ellipses satisfactorily. To restore the ellipses from one spectrum line to another is equivalent to a motion of the micrometer over $N_c - N_c' = \Delta N_c$. This constitutes a second method of interferometry of lower sensitiveness; *i. e.*, a coarse adjustment on the number of fringes which pass a given spectrum line. Per fringe or per vanishing ring, obviously, the displacement of the mirror on the micrometer will be a half wave-length of the part of the spectrum in question.

I may add, in conclusion, that I have recently* constructed a displacement interferometer combining the desideratum of lightness and portability with rigidity, and provided with long arms of invariable length (water circulation within), and with sufficient height of mirrors, &c. above the arms to admit of the insertion of bulky objects like a fog-chamber into the interfering beams of light. The adjustment of fig. 8 is particularly useful, the distance M to N being one or more metres. The apparatus is especially adapted for the measurement of the refraction of gases at all temperatures and conversely (in view of the large coefficient) for the measurement of high temperature in terms of the refraction of gases. It is also adapted for the measurement of the pressure variation of the refraction of a gas and conversely for pressure measurement in terms of refraction, particularly in case of the adiabatic transformations of a dry or a wet gas, at all temperatures. For the displacement of ellipses is instantaneous and dependent on the ratio of pressure to absolute temperature. Tests made with the fog-chamber have given results which promise to be fruitful, as will be shown elsewhere.

Brown University,
Providence, R.I.

XCV. *On Mr. McC. Lewis's Papers on the Internal Pressure of a Liquid.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

MR. MCC. LEWIS, in his voluminous and interesting papers†, departs from Dupré's proposition, according to which the latent heat of vaporization of a unit of volume is equal to the internal pressure, and concludes in applying the second law of thermodynamics to this case, that "apparently the only accurate relation, the thermodynamic one," is

$$K - l = T \left(\frac{\partial K}{\partial T} \right)_v \quad . \quad . \quad . \quad . \quad . \quad (1)$$

"But," according to Mr. McC. Lewis, "this does not allow us to go further unless some new assumption be made with

* Am. Journ. Science, xxxiii. p. 109 (1912).

† Phil. Mag. xxii. pp. 193-197, and pp. 268-276 (1911). Trans. of Faraday Soc. vii. pp. 94-115 (1911). *Zeitschr. f. phys. Chem.* Bd. lxxviii. pp. 24-38 (1911).

respect to K and T . In the absence of anything better, I would tentatively suggest as a working hypothesis—

$$\frac{1}{K} \frac{\partial K}{\partial T} = \frac{1}{l} \frac{\partial l}{\partial T} \dots \dots \dots (2)^{**}$$

This working hypothesis cannot be considered as convenient at least for a great interval of temperature, for upon integrating equation (2) we obtain †

$$K = C_1 l \dots \dots \dots (3)$$

After substituting (3) in (1) we obtain further

$$C_2 K = T \left(\frac{\partial K}{\partial T} \right)_v \dots \dots \dots (4)$$

$$K = f(v) T^{C_2} \dots \dots \dots (5)$$

$$l = C_3 f(v) T^{C_2} \dots \dots \dots (6)$$

It is difficult to consider these (3), (5), (6) equations as true for the sole reason, that at T_K (critical temperature) $l=0$,

but $K = \frac{a}{v_K^2}$, which is not zero.

But the introduction of any working hypothesis may be superfluous. This will be obvious, if we remember the deduction of equation (1)†. The fundamental assumption of this deduction is that b is independent of temperature. If b is dependent on temperature, we obtain on differentiating the van der Waals' equation with respect to T , keeping the volume constant,

$$\left(\frac{\partial p}{\partial T} \right)_v = \frac{R}{v-b} \left[1 + \frac{T}{v-b} \left(\frac{\partial b}{\partial T} \right)_v \right] - \left(\frac{\partial K}{\partial T} \right)_v.$$

Mr. McC. Lewis has neglected $\frac{T}{v-b} \left(\frac{\partial b}{\partial T} \right)_v$ compared with 1.

It is true that van der Waals assumes $\left(\frac{\partial b}{\partial T} \right)_v = 0$ §, but he supposes also $\left(\frac{\partial a}{\partial T} \right)_v = 0$.

The van der Waals' equation does not respond to the observed facts with sufficient precision within large limits.

* Trans. of Faraday Soc. vii. p. 113. Cf. Phil. Mag. xxii. p. 194.

† In the following C_1, C_2 , etc. mean constants.

‡ Phil. Mag. xxii. p. 269.

§ *Lehrbuch der Thermodynamik*, von v. der Waals, 1908, p. 78—"... lässt sich zeigen das die Einführung von a als Temperaturfunktion mit der innern latenten Verdampfungswärme in Konflikt kommt." *Ibid.* p. 80—"Eine Abhängigkeit von b von der Temperatur wird durch diese Ueberlegung unwahrscheinlich gemacht."

This is quite obvious from the numerous attempts to correct it or to deduce another equation. I will mention only Boltzmann's deduction, that $C = C' e^{\frac{C}{T}}$, and the equation in the form given by Lorentz:

$$\left(p + \frac{f(T)}{v^2}\right)v = RT \left(1 + \frac{b}{v} e^{\frac{C}{T}}\right).$$

Hence it follows, that the proposition of Mr. McC. Lewis that "internal work and internal energy can be treated with respect to one another in the same way as external work and internal energy" * is, perhaps too risky—of which the author was, however, quite aware when saying "it must be remembered, however, that thermodynamic work terms are essentially external work terms" †.

By trying to give a physical meaning to each member of equation (1), it results that $-T \left(\frac{\partial K}{\partial T}\right)_v$ expresses the excess of kinetic energy of the molecules of vapour over the liquid ones at the same temperature, which, however, may appear doubtful. We cannot assume any other meaning, K being "le travail total de désagrégation," provided Mr. McC. Lewis follows Dupré's idea. It is also doubtful whether "the equality [of the internal energy change to internal work] would only hold good if K were independent of temperature" ‡. Dupré says §: "Ainsi le travail restant à accomplir pour séparer complètement les molécules à température constant est en raison inverse du volume; son expression général est le produit de l'inverse du volume par une fonction de la température seule" ||, and gives the following equation:

$$(282) \quad \lambda = p(v_1 - v_2) + K - K' ¶,$$

where λ is latent heat of vaporization (per 1 gr.), $p(v_1 - v_2)$ external work, and K, K' total work of disaggregation in the liquid and gaseous states.

Yours faithfully,

W. SUKHODSKI.

Laboratory of Physical Chemistry,
Polytechnical Institute,
St. Petersburg, Russia.

* Trans. of Faraday Soc. vii. p. 113.

† Ibid. p. 96.

‡ Phil. Mag. xxii. p. 194.

§ *Ann. de Chim. et Phys.* 4 ser. vol. vi. (1865) p. 286.

|| Cf. Phil. Mag. xxii. p. 193. Dupré virtually assumed K independent of temperature.

¶ *Ann. de Chim. et Phys.* vol. vi. p. 283. I write it in the modern designations.

XCVI. *The Solubility of Calcium Carbonate in Water.* By
JAMES KENDALL, M.A., B.Sc., Vans Dunlop Scholar in
Chemistry, University of Edinburgh*.

THE determination of the solubility of calcium carbonate in water is evidently, apart from its purely chemical interest, a very important problem, owing to the application of the values obtained to the results of water analysis, and to their bearing upon the study of geological formations. Although much work has been done upon the subject, no satisfactory measurements have been made. The main difficulty in the determination of exact results lies in the fact that, in consequence of the extremely small degree of solubility, it has been necessary to adopt indirect methods for its estimation. Thus Kohlrausch and Rose (*Zeit. phys. Chem.* xii. p. 234 (1893)) included calcium carbonate in their investigations on the solubility of difficultly-soluble substances in water by means of the electrical conductivities of the saturated solutions. Calcite, arragonite, and the amorphous form of the carbonate were examined at temperatures ranging from 2° C. to 34° C., and provisional figures for the solubilities and temperature coefficients were given. The method and its application were further elaborated in a second paper published ten years later (*Zeit. phys. Chem.* xlv. p. 197 (1903)); but in the final paper (*Zeit. phys. Chem.* lxiv. p. 129 (1908)), giving the calculation of the actual solubilities of the substances examined from the observed conductivities, the figures for all carbonates were omitted. This was because the errors introduced by the correction necessary for the conductivity of the water itself may be greatly augmented owing to our lack of knowledge of the influence of the $\text{CO}_3^{''}$ ion. Any values obtained could therefore only be regarded as rough approximations. The provisional figures of the first paper were consequently retained.

Holleman also, simultaneously with Kohlrausch and Rose (*Zeit. phys. Chem.* xii. p. 125 (1893)), applied conductivity measurements to the determination of the solubility of calcium carbonate, and obtained similar results.

Foote (*Zeit. phys. Chem.* xxxiii. p. 740 (1900)), using other indirect methods to determine the ratio of the solubilities of the two crystalline forms, confirmed the provisional figures of Kohlrausch in this respect, but made no actual solubility measurements.

In water analysis, the determination of the amount of calcium bicarbonate present in a given sample (*i. e.*, the

* Communicated by Prof. J. Walker, F.R.S

degree of the temporary hardness) is a matter of great importance. If the sample is boiled for some time the dissolved carbon dioxide is expelled, and the greater part of the temporary hardness is destroyed by precipitation of the calcium carbonate, but some will still remain in solution. The amount of this must be known before the values of the temporary and permanent hardness of the water can be calculated; it has been roughly estimated at .02 gr. per litre. Measurements of the solubility of calcium carbonate at other temperatures and under ordinary conditions are altogether lacking.

At the suggestion of Professor Walker, I have attempted the direct estimation of the solubility of calcium carbonate in water. Experiments have been made, at temperatures between 25° C. and the boiling-point, upon all three varieties of the substance—calcite, arragonite, and the amorphous form; also upon solutions of the bicarbonate, in equilibrium with air free from carbon dioxide and with atmospheric air.

The method of procedure was, briefly, as follows:—a large volume—2 to 3 litres—of the saturated solution was prepared in a large silica flask, and filtered off into a second silica flask containing a small excess of acid; the liquid was evaporated to small bulk—50 to 100 c.c.—and titrated against a known solution of baryta.

It is the use of silica vessels that renders this direct determination possible; with glass or porcelain vessels the solution would dissolve out alkali, during concentration, sufficient to vitiate the results entirely. The silica flasks used were of three to four litres capacity; their resistance to neutral, acid, and alkaline solutions of the concentrations existing in the subsequent experiments was first tested as below.

Neutral Solution.—Water of specific conductivity 1.25×10^{-6} can be obtained by one distillation from tap-water by the addition of 10 c.c. Nessler's solution to two litres of water. Jena glass vessels and a tube of pure tin, fitted with a condenser, are employed; the distillation is carried out in the open air, and the first third of the distillate rejected. On redistillation of this water from one silica vessel to another, by means of a silica hood carefully ground on the neck of the first vessel, water of a specific conductivity $.85 \times 10^{-6}$ was obtained. If half of this distillate be boiled away, the residue possesses a specific conductivity of $.70 \times 10^{-6}$, which is the conductivity value for the purest water that can be obtained in contact with air. This shows conclusively that pure water dissolves no conducting material from a silica vessel.

Acid Solution.—10 c.c. of decinormal sulphuric acid were added to about two litres of water in one of the vessels, and the solution evaporated down to 50 c.c. On titration against baryta, with phenolphthalein as indicator, the existence of the original amount of acid in the solution (within limits of experimental error) was established.

Alkaline Solution.—Two litres of calcium hydroxide solution of concentration $\cdot 001$ N were boiled in the silica vessel for some time, and then, after a known excess of sulphuric acid had been added, evaporated to small bulk. On titration against baryta, with phenolphthalein as indicator, the required excess of acid was found to exist in the solution.

The silica flasks are therefore not attacked, to any appreciable extent, by solutions of the above concentrations, and these were never exceeded in subsequent experiments.

The sulphuric acid used throughout was of approximately decinormal concentration, the baryta solution of approximately centinormal. Phenolphthalein was employed as indicator. All water used was freshly distilled, and collected directly into one of the silica flasks.

Mineral Calcite and Arragonite.

The calcite used consisted of large, transparent crystals of iceland-spar (density 2.72); the arragonite was a fine museum specimen (density 2.90), which showed no traces of strontium when tested by the spectroscope. Both minerals were finely powdered in an agate mortar. Successive experiments with the same sample of solid led to constant solubility results—a most rigorous test of purity. Experiments were carried out at three temperatures: 25° C., 50° C., and 100° C.

For the determinations at 100° C. a small quantity of the powdered substance was added to water at the boiling-point, and after the boiling had been continued for periods varying from 40 to 200 minutes, the solution was filtered off from the remaining solid. For those at 50° C. and 25° C. the silica vessel was immersed in a thermostat at the particular temperature, and fitted with a rubber cork, through which passed two silica tubes, one short and the other reaching to the bottom of the flask. The solution could thus be kept agitated by a current of pure air drawn through the apparatus; the air being led, from outside the building, through a long tube packed with cotton-wool, a wash-bottle containing Nessler's solution, two soda-lime towers, and finally a wash-bottle containing pure water, before entering the solution. Equilibrium was established much more slowly at these

lower temperatures; the solutions were tested at different periods until a steady solubility value was reached.

The manner of filtration at the boiling-point occasioned a great deal of difficulty. Simple filtration through a double-walled porcelain funnel, fitted with a hardened fluted filter-paper, and heated without by a water-jacket, was first attempted; but no satisfactory results could be obtained. Although the filtration was carried out as rapidly as possible, the amount of evaporation from the filtrate was necessarily considerable, and further, the solution exerted an appreciable solvent action on the funnel itself, as was found by testing with solutions of prior known concentration. At the lower temperature also, open filtration could not be employed, since the short exposure of the solution during filtration to the carbon dioxide of the atmosphere led to a remarkable increase in the solubility value obtained.

The method of upright filtration was therefore adopted. The solution was drawn by suction from the first to the second silica vessel through a tube of pure tin, in the shape of an inverted U, one arm of which was longer than the other. The longer arm dipped into the solution, and was closed at the end by means of a double layer of hardened filter-paper, protected on both sides by squares of muslin, the whole being tied tightly to the tin tube by means of linen thread upon a rubber band. The shorter arm was fitted to the second vessel with a rubber cork, through which passed a silica tube leading to the pump. A glass flask, immersed in ice-cold water, was interposed as a condenser to intercept water vapour coming over from the hot filtrate.

By this method, using a tube of one-inch diameter, two litres of solution could be filtered over in a quarter of an hour. Loss of water from the filtrate by evaporation, and exposure to the air during filtration, were both avoided, and for a short time concordant results were obtained. After a few experiments, however, the hot solution began to attack the tin tube, and once the surface of this was worn away, the action increased rapidly. In the case of experiments at the boiling-point, the filtrate, instead of being clear, was quite cloudy on concentration, and, when tested, showed a decided trace of tin.

The tin tube was therefore discarded for a similar tube of silica, and with this satisfactory results at 100°C . were obtained. At the lower temperatures no noticeable action was exerted by the solution upon the tin tube, and this was

therefore used at these temperatures on account of its greater convenience. A rubber cork, through which passed a short silica tube, being fitted to each arm of the tube, pure air was drawn through the solution during the whole period of filtration.

Immediately after filtration, and before cooling, the amount of liquid filtered over was ascertained by direct weighing. It was found by experiment that the difference in weight obtained by weighing when hot, and by weighing after closing the mouth of the vessel and allowing to cool, was between 1 and 2 grammes. This, with a filtrate of 2 litres, introduces an error of less than .1 per cent., which is negligible. The saving of time is very great, as the solution requires at least two hours to cool to the ordinary temperature, and another half-hour to be brought to the boiling-point again. The actual evaporating down of the solution takes two to three hours, being conducted rapidly at first and more slowly as the volume decreases. When 50 to 100 c.c. remain, the vessel is allowed to cool, and the amount of the residue found to within .1 gramme by weighing.

The silica vessels remained practically constant in weight throughout the whole series of experiments.

The calculation of results is very simple, since all the solutions are so dilute that their densities may be taken as equal to that of water at the same temperature. Thus, if 2000 grammes of solution be added to 10 c.c. $\frac{N}{10}$ acid, and evaporated down to 50 grammes, and it is found that 1.53 c.c. $\frac{N}{100}$ baryta solution are required to neutralize 25 c.c. of the residue, we have

$$\frac{10(1) - 2000 x \cdot a}{50 b} = \frac{.01 \times 1.53}{25},$$

where x is the normality of the solution, and a and b the number of cubic centimetres occupied by one gramme of water at temperature of filtration and at the ordinary temperature respectively.

The results thus obtained in normalities are transformed in the tables given below into grammes per litre, and the figures of Kohlrausch are appended for comparison.

All experiments were performed at least in duplicate, in some cases they were repeated many times. This was

necessary since, on several occasions, single results were not confirmed on repetition; indeed, the general experience throughout was that, at any time, and for no apparent reason, a false result was liable to be obtained. Further, when results in agreement were obtained, the degree of accuracy was usually not closer than within 2 per cent., whereas the limits of error should not amount in all to 1 per cent.

The causes of this are, I think, as follows. Firstly, there is the extreme difficulty of keeping the silica vessels and filtering apparatus chemically clean. The amount of surface is necessarily very large, a great deal of handling has to be done in the course of an experiment, and the slightest trace of acid or alkali introduced on the tube or the interior of the vessels would be sufficient to spoil a result. The surface of the silica vessels is very rough, and particles of solid are washed out only with great difficulty. Thus, in using a vessel for arragonite which has been employed for calcite, it is not sufficient to wash out, or even to boil out, with water; the vessel must be boiled out first with dilute acid for a long time, and then with successive quantities of water.

As an illustration of the reality of danger of error from this source, it may be pointed out that the introduction of .001 gr. of alkali (calcium carbonate) is sufficient to cause an error of from 5 to 10 per cent.

The silica vessels were therefore most scrupulously cleaned out before each set of experiments, the filtering apparatus before each single experiment. The filter-paper and muslin squares were changed after each determination.

A second source of error is the presence of a trace of carbon dioxide in the water used. As this reappears, however, in a much greater degree, in the course of subsequent experiments, it will be discussed later.

The results for calcite and arragonite at 25° C., 50° C., and 100° C. are given below, both in tabular and in graphic form. At the two lower temperatures the thermostat was kept constant within 0°·1 C.; the figures given for 100° C. are those obtained at the boiling-point, the barometric pressure being observed at the time of the experiment. The true temperature was usually a few tenths of a degree lower than 100° C., but, as will be seen from the diagram, the temperature coefficient is so small that the results are substantially correct for that temperature. The diagram also shows the solubility curve for calcite under ordinary atmospheric conditions (see page 973),

Mr. J. Kendall on the Solubility of
Calcite.

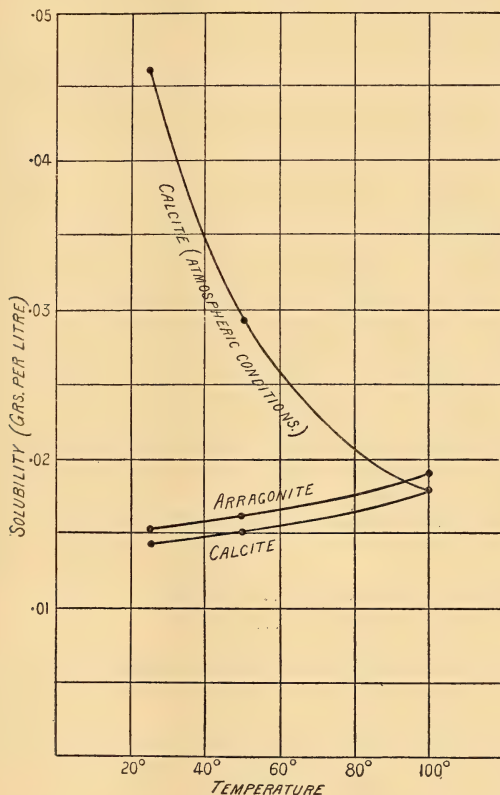
Temperature.	Time before filtration.	Grs. per litre dissolved.			Mean result.	Kohlrausch.
25° C.	1 day	·01428	·01440	}	·01433	·014
	2 days	—	·01433			
	3 days	·01431	—			
50° C.	1 day	·01507	·01506	}	·01504	·016
	2 days	·01491	—			
	3 days	—	·01513			
100° C.	40 mins.	(·01816)	·01785	—	·01779	—
	60 mins.	(·01819)	·01770	·01777		
	80 mins.	(·01810)	·01776	—		
	120 mins.	(·01804)	·01785	·01780		

Arragonite.

Temperature.	Time before filtration.	Grs. per litre dissolved.		Mean result.	Kohlrausch.
25° C.	6 days.	(·01075)	—	·01528	·016
	10 days.	(·01286)	—		
	6 days.*	(·01511)	—		
	10 days.*	·01524	·01530		
	12 days.*	·01522	·01536		
50° C.	3 days.	(·01206)	—	·01617	·018
	6 days.	(·01572)	—		
	3 days.*	(·01608)	—		
	6 days.*	·01616	·01611		
	8 days.*	·01616	·01624		
100° C.	60 mins.	(·01178)	—	·01902	—
	120 mins.	(·01660)	—		
	180 mins.	·01926	—		
	60 mins.*	·01901	·01890		
	120 mins.*	·01919	·01898		
	180 mins.*	·01902	·01879		

The results for calcite at 100° C. that are placed between brackets are those obtained with the tin tube ; although they agree well together, they are slightly higher than those found when using the silica tube, and are not employed in the calculation of the mean value. The results which are bracketed together are those obtained from experiments with successive portions of the same solution at different times ; by this means it could be ascertained when the final solubility value had been reached, in the case of solutions only slowly attaining equilibrium.

It will be seen that arragonite is far slower in attaining equilibrium in solution than calcite. Indeed, in order to obtain results in a reasonable time, arragonite was taken not with water but with a saturated calcite solution, carefully



filtered free from solid. Thus, the solution being already almost saturated with regard to arragonite, the end point was reached much more quickly. Experiments performed in this manner are distinguished by a star in the table. Where it is evident that the true solubility value has not been reached, the result is placed between brackets and is not used in the calculation of the mean value.

The comparative slowness with which equilibrium is attained in the case of arragonite is not due to the larger size of the particles, for by observation with the microscope it was found that the two minerals were ground to equal degrees of fineness, but may rather be ascribed to the

greater density of the arragonite, offering more resistance to the solvent action of the water.

The results for arragonite are, in general, less concordant than those for calcite; this is due to the instability of the former. Observations with the microscope were made on slides of the solid residue from each experiment; calcite was always unchanged, but arragonite at 100° C. always showed a few crystals of calcite, the rhombic crystals of the latter being easily distinguishable among the needle-shaped crystals of arragonite. The proportion of calcite present, although always very small, increased regularly with the time of boiling, and thus a true solubility value for arragonite was never attained, but an intermediate value between the solubilities of the two minerals. At 50° C. and 25° C., no change of arragonite to calcite was observed.

The values obtained are in good agreement with those of Köhlrausch at the ordinary temperature. The ratios of the two solubilities at different temperatures are also fairly concordant with the results of Foote (*Zeit. phys. Chem.* xxxiii. p. 740 (1900)). It will be seen from the diagram that the two curves run almost parallel; any transition point is obviously either far above or far below the ordinary temperature, if it exists at all. The ratios of the solubilities are $\left(\frac{\text{arragonite}}{\text{calcite}}\right)$:—

	25° C.	50° C.	100° C.
Observed	1.064	1.075	1.069
Foote (by interpolation) ...	1.130	1.114	—

Foote has concluded, from the decrease of the ratio obtained with rise of temperature, that the inversion temperature is above the ordinary range; the above results, however, show a constant ratio, and hence, since the solubility increases with the temperature, greater difference of solubility with rise of temperature.

It is an interesting point that the ratio of the specific gravities of the two forms is $\frac{2.90}{2.72} = 1.066$. The ratio of concentration in the solid form to concentration in the solution thus appears to be constant for the two varieties.

Calcium Bicarbonate Solutions.

The presence of carbon dioxide increases the solubility of carbonates in water to a marked degree, owing to the formation of soluble bicarbonates. The equilibrium of the system is determined by the partial pressure of the carbon dioxide over the solution; and in the case of calcium

carbonate here considered, a very small proportion of carbon dioxide corresponds to an enormous increase in the solubility. For this reason, it has been possible to investigate, by the ordinary methods, the equilibrium of the system even for very small partial pressures of carbon dioxide (Schloesing, *Compt. rend.* lxxiv. p. 1552 (1872); Treadwell and Reuter (*Zeit. anorg. Chem.* xvii. p. 170 (1898)). Beyond a certain limit, however, the results become too inaccurate, owing to the diminished solubility. The equilibrium under ordinary atmospheric conditions, for example, which is of importance in water analysis, cannot be determined by the usual volumetric methods.

If a current of air free from carbon dioxide be drawn through a bicarbonate solution, equilibrium is re-established by precipitation of carbonate, and this precipitation will continue until all bicarbonate disappears from the solution, *i. e.*, until all free carbon dioxide is removed. There will therefore remain a saturated solution of calcium carbonate.

Much confusion has always existed in regard to the state in which calcium carbonate falls out of solution. The precipitate obtained differs according to the concentration of the solution, the rate at which precipitation occurs, the temperature of experiment, the partial pressure of carbon dioxide above the solution, and the presence of other salts. The most complete experiments are those of Rose (*Jour. prak. Chem.* lxxxi. p. 383 (1860); lxxxii. p. 351 (1861)). From bicarbonate solutions above 90° C., arragonite is deposited; between 90° C. and 30° C., a mixture of calcite and arragonite; under 30° C. only calcite. The stability of the arragonite varies according to the conditions of formation.

By double decomposition between concentrated solutions of a calcium salt and a carbonate in the cold, amorphous calcium carbonate is said to be precipitated, transformation to calcite following. The formation of a third crystalline form, also unstable, has lately been described by Meigen (*Chemiker-Zeitung*, xxxiv. p. 1015 (1910)).

In the experiments described below the primary object was to determine the degree of solubility of the carbonate, by the complete withdrawal of the carbon dioxide from bicarbonate solutions, at the temperatures of 25° C., 50° C., and 100° C. The values obtained would, it was expected, give some indication of the form in which precipitation had occurred, and also check the figures for the solubility of calcite and arragonite previously obtained.

The direct preparation of the bicarbonate solutions, by

bubbling carbonic acid gas through water containing finely powdered carbonate in suspension, could not be employed. The solution of the crystalline carbonate under these conditions is very slow, and it is essential, to ensure that the precipitate to be obtained afterwards shall be naturally deposited, that no trace of solid carbonate should be present in the liquid.

The solution was therefore prepared as follows. Finely-powdered calcite was converted into lime by roasting in a platinum crucible, and transferred to a flask of Jena glass, filled with water. A second flask was half filled with water through which carbon dioxide had been bubbled for about ten minutes. To this the lime water was added in a slow stream by filtration. A hardened filter-paper was used, supported in a funnel with a long stem, drawn out to a fine jet, dipping into the water. As the liquids met a fine, cloudy precipitate was produced, which immediately dissolved on shaking the flask. The solution could be kept clear only by means of constant agitation; if the precipitate was once allowed to settle, it assumed a hard, crystalline form and was most difficult to dissolve. The addition of the lime-water was stopped before the solution became saturated with bicarbonate, as soon as the precipitate began to be slow in disappearing.

The solution was now added to a large excess of water contained in one of the vessels. The water in the silica flask was maintained, during this addition, at the temperature of the subsequent experiment, and the bicarbonate solution was added slowly, so that any immediate precipitation of carbonate took place at the required temperature. This was of special importance in the case of solutions at the boiling-point. The experiments were now carried on exactly as previously described. At 25° C. and 50° C. the silica flask was suspended in a thermostat and air free from carbon dioxide drawn through the solution; at 100° C. the carbon dioxide was expelled by boiling. Supersaturation was very liable to occur at the lower temperatures, unless the solution was made concentrated enough to give a large excess of calcium carbonate on removal of the carbon dioxide.

The precipitates obtained were always tested by the microscope, and examination showed :—

- | | |
|--------------------------|---|
| at 25° C. | rhombic crystals only. |
| at 50° C. | an intimate mixture of rhombic
and needle-shaped crystals. |
| at 100° C. | needle-shaped crystals, with a
very few rhombic. |

This is in agreement with the results of Rose—that, at 25° C., calcite is obtained; at 100° C. arragonite, slowly transforming into calcite; at 50° C. a mixture of the two forms.

Nevertheless the previous solubility values were not confirmed. At 25° C. and 50° C., equilibrium was established so slowly that the final value could not be determined, the fall in concentration being extremely slow; at 100° C., a fairly constant value was obtained; this, however, was much higher than the value found for arragonite at 100° C. Examples of the results obtained, with the times of experiment, are given below, expressed as before in grammes per litre.

	25° C.		50° C.	
3 days	·03444	·03097	·02861	—
5 „	·03421	—	·02635	·02692
9 „	—	·02962	—	·02480
100° C.				
40 mins.	·02511	—		
80 „	·02331	·02329		
120 „	·02346	·02333		
180 „	·02309	—		

The explanation of the results at 100° C. was at first thought to lie in the fact that the needle-shaped crystals precipitated were not, as has been held, identical with mineral arragonite, but were another modification of the carbonate (compare Meigen on the formation of “Vaterite,” *Chemiker-Zeitung*, xxxiv. p. 1015 (1910)). This view seemed to be confirmed by the action of cobalt nitrate upon the precipitate.

The differences of behaviour of the various forms of calcium carbonate with boiling cobalt nitrate solution have been examined, qualitatively and quantitatively, by Meigen (*Central-blatt*, ii. p. 1128 (1901); *Chemiker-Zeitung*, xxxiv. p. 1015 (1910)). When finely-powdered arragonite is boiled with a dilute solution of cobalt nitrate, a lilac-coloured precipitate is quickly produced; in the case of calcite, the action is much slower, and the precipitate is tinted blue. Presence of other metallic salts in the solution confuses those colour reactions.

The precipitated crystals gave, when the test was applied, an immediate flocculent lilac-coloured precipitate. Mineral calcite and arragonite, powdered to the same degree of fineness (as observed by the microscope), were only slightly tinted after boiling for some minutes, and no noticeable precipitate was formed.

The specific gravity of the precipitated crystals was found, however, by the Westphal balance to be identical with that of arragonite, 2.89.

The higher values obtained at the lower temperatures of 25° C. and 50° C. are clearly to be accounted for by the obstinate retention of the last trace of carbon dioxide by the solution, equilibrium never being attained in the time of experiment. This was found to be also the case at 100° C. When the experiments were conducted as before until a precipitate had formed, and then all the liquid decanted off, fresh water added to the crystals remaining, and the experiment continued as before, the following solubility values were obtained.

	25° C.	50° C.
4 days	·01879 }	·01958 }
6 days	·01868 }	·01976 }
	100° C.	
60 mins.	·02271	
120 mins.	·02238	

These are still, it will be seen, much higher than those previously found for calcite and arragonite; the value at 100° C. is scarcely lowered at all. The curve of the solubility has now, however, become approximately parallel to those given by the two crystalline varieties.

Further investigation showed that decantation is insufficient to remove the final trace of carbon dioxide. It is necessary to shake up thoroughly the crystals that remain with successive quantities of water, before proceeding with the experiment; and by this means constant results were finally obtained, comparable with those previously found for the mineral calcite and arragonite.

	25° C.	Mean result.
2 days	·01450 }	
5 days	·01464 }	·01466
	50° C.	
2 days	·01554 }	·01549
5 days	·01536 }	—
	100° C.	
60 mins.	·01909	·01917
120 mins.	·01899	·01911
		·01909

It will be seen that the results of the experiments at 25° C. are substantially the same as those for mineral calcite at that temperature; those at 50° C. lie between the values

for calcite and arragonite; those at the boiling-point are identical with the value for arragonite at the boiling-point.

There is still a difference of 1 to 2 per cent. in the values obtained by the two methods; this must be attributed to a minute trace of carbon dioxide, not removed by the washing. It is probably the carbon dioxide that remains, as it were, adsorbed on the surface of the crystals that causes the different behaviour with cobalt nitrate solution.

From the above it will be evident that the accuracy of the method depends entirely upon the purity of the water used for experiment, a trace of carbon dioxide being sufficient to raise the solubility of the carbonate very appreciably. In all experiments the water used was freshly distilled into one of the siclia flasks, yet it would always contain a small amount of carbon dioxide, and small differences in this amount would be sufficient to affect the constancy of the results.

Amorphous Calcium Carbonate.

The conditions for the precipitation of calcium carbonate in its amorphous form have already been discussed. In the dilute solutions employed for the experiments with bicarbonate solutions, one or other of the crystalline forms was always obtained; only in the preparation of the solutions was the amorphous form obtained as a cloudy precipitate, which immediately, unless dissolved, transformed into a crystalline form, calcite.

The amorphous form is the most unstable of the three varieties of the carbonate, and its solubility is necessarily higher than those of the other forms. Nevertheless, the figures given by Kohlrausch (*Zeit. phys. Chem.* xii. p. 234 (1893)) are identical with those for calcite. It is evident that transformation of the amorphous form to calcite had occurred in the course of the experiment.

Similar results were obtained in the direct determinations given below. Experiments were carried out both with natural and prepared forms. The former consisted of ordinary soft chalk; the latter was obtained by heating finely-powdered calcite to lime in a platinum crucible, and reforming the carbonate by means of a current of carbon dioxide passed over the slowly-cooled oxide. The experiment was carried out quantitatively to ensure the absence of unchanged calcite—the heating being continued until the loss of weight was equal to the theoretical. The cooling in a current of carbon dioxide was also repeated until the original weight was restored, in order to remove all traces of quicklime. The experiments were carried out exactly as before,

at the temperatures of 25° C., 50° C., and 100° C., and results are given below in grammes per litre.

Prepared Carbonate.

		25° C.	Mean result.
2 days		·01445 }	·01445
3 days		·01436 }	
		50° C.	
2 days		·01510 }	·01515
3 days		·01521 }	
		100° C.	
60 mins.		·01824	·01816
100 mins.		·01809	
		Soft Chalk.	
		100° C.	
60 mins.		(·02117)	·01777
100 mins.		·01769	

It will be seen that the figures are the same as for calcite. The experiments with soft chalk were carried out by treating a quantity with successive portions of water—the first high value is due to the removal of impurities.

The amorphous form is hence seen to be extremely unstable, and no figures for its solubility can be obtained. Another method of preparation—heating the precipitated oxalate to oxide and converting to carbonate by slowly cooling in a current of carbon dioxide—led to the same solubility values being obtained. Conversion to calcite takes place either as soon as the carbonate is formed at the high temperature, or else as soon as it is brought in contact with water. The powdered substance shows, under the microscope, no signs of crystalline character; its density is, however, the same as that of calcite (2·70 by the Westphal balance). For this reason no change in volume could be observed when a dilatometer was packed with the powder and water drawn in to fill the bulb.

Solubility under Atmospheric Conditions.

The extremely small proportion of carbon dioxide in ordinary air is sufficient to raise the solubility of calcium carbonate at the ordinary temperature several hundred per cent. It is therefore necessary to know accurately the amount of carbon dioxide in the air at the time of experiment to render the results, which are of special importance for their applications to water analysis and geology, of any value.

The method of estimation employed was that of Pettenkofer, as improved by Walker (J. C. S. lxxvii. p. 1110 (1900)). By its use the proportion of carbon dioxide in the atmosphere could be determined accurately within $\cdot 1$ part in 10,000; the determinations actually made varied from 3.56 to 3.88 parts in 10,000, with an average value of 3.69 parts in 10,000.

This value can be taken as the conditions for all experiments given below, for by observation it was found that the final equilibrium of the solution was established so slowly that constant results were obtained in spite of slight changes in the carbon dioxide values from day to day. For the same reason small changes in the barometric pressure had no effect on the solubility values obtained; the mean barometric height was 754 mm.

The experiments were performed at 25° C. and 50° C. as before; powdered calcite was taken in the silica flasks with freshly distilled water, and atmospheric air led through the solution, after being passed through a long tube filled with cotton-wool to remove all dust. The results are given below, in grammes per litre, and are also shown in graphic form upon the diagram on page 965.

	25° C.	Mean value.
3 days	(.04351)	.04608
5 "	(.04545)	
18 "	.04607	
19 "	.04592	
21 "	.04625	
	50° C.	
4 days	(.02911)	.02925
7 "	.02930	
9 "	.02935	

The solubility at 25° C. is hence seen to be more than three times as great as that in pure air (.04608 and .01433 gr. per litre respectively); that at 50° C. is nearly twice as great (.02925 and .01504 gr. per litre respectively). At 100° C. the two values should be identical (.01779 gr. per litre). A reference to the diagram (page 965) will show clearly the remarkable difference in the characters of the two solubility curves.

At the ordinary temperatures a bicarbonate solution would give the same values as calcite, since the precipitation takes place in that form. Mineral arragonite would be, as in pure air, slightly more soluble, but the exact determination of the value is of little importance, the results given above being all that are required for practical use.

Conductivity of Bicarbonate Solutions.

The importance of measurements of electrical conductivity in the determination of the purity of a sample of water, and especially in the discovery of any sudden change in the degree of hardness or in the salt content of a town supply, has only recently been recognized. An apparatus for the above purpose (the Dionic Water Tester) is already in the market.

The introduction of the measurement of electrical conductivities into water analysis has rendered necessary the accurate determination of the conductivities of bicarbonate solutions. The values for calcium bicarbonate are clearly of special importance.

The conductivity of solutions of sodium bicarbonate has been investigated by Walker and Cormack (*J. C. S.* lxxvii. p. 10 (1900)) for the purpose of determining the velocity of the HCO_3' ion. Experiments were carried out at 18°C . between dilutions of 32 and 512. Within this range no difference was observed between solutions diluted with pure water and with water saturated with carbon dioxide.

In the following experiments the dilution was carried further, solutions being used from $v=10$ to $v=10,000$, at a temperature of 25°C . The conductivities were determined in a Cantor cell, with the use of a rotating commutator and a galvanometer. Much more accurate values can be obtained by this method for dilute solutions than with the usual induction-coil and telephone.

Sodium bicarbonate solution was made up by bubbling excess of carbon dioxide through sodium hydroxide solution, freshly prepared from metallic sodium. The solution was standardized both volumetrically by neutralization with a known solution of hydrochloric acid, and gravimetrically, by neutralizing 100 c.c. with hydrochloric acid in a platinum basin, evaporating carefully to dryness, and weighing the residue.

Two series of dilutions were made, one with pure water, the other with water containing excess of carbon dioxide. The pure water was prepared by distillation, in the open air, of water to which a little Nessler's solution had been added, as described before; its specific conductivity was 1.10×10^{-6} . The correction for the water conductivity is made as follows. The part due to carbonic acid is, at most, $.70 \times 10^{-6}$ (Walker and Cormack, *J. C. S.* lxxvii. p. 11 (1900)). The influence of this on the bicarbonate solutions is negligible up to very high dilutions. The remaining conductivity, $.40 \times 10^{-6}$, is directly subtracted from the observed values, as below. The values given are the equivalent conductivities of the solutions, expressed in reciprocal ohms.

Conductivity of NaHCO_3 . $v = 10.07$ (volumetrically); 10.08 (gravimetrically).

V.	With pure Water.		With Water containing CO_2 .
	Uncorrected.	Corrected.	
10.07	76.3	76.3	76.5
20.15	80.8	80.8	81.0
40.3	84.6	84.6	84.8
80.6	87.4	87.4	87.8
161.2	89.8	89.7	90.1
322.4	91.7	91.6	92.1
645	93.4	93.1	94.2
1290	94.6	94.1	98.3
2580	95.9	94.9	107.5
5160	98.2	(96.1)	137.3
10320	101.7	(97.6)	—
∞	—	97.0	—

It will be seen that the two series are practically identical up to the limits investigated by Walker and Cormack. At the higher dilutions, however, the presence of the excess of carbonic acid in the solution gives rise to a rapidly-increasing conductivity value. This is due to the ionization of the carbonic acid, which is quite appreciable in the more dilute solutions.

The corrected values for the first series lead to a conductivity value at infinite dilution of 97.0. At the two highest dilutions hydrolysis has evidently begun to be appreciable. The velocity of the HCO_3' ion is therefore found to be, taking the velocity of the sodium ion as 51.0, equal to 46.0.

Calcium bicarbonate solution was made up as previously described, the requisite volume of lime-water of known concentration being run into water containing carbon dioxide to give a solution of dilution 32. This was too unstable at 25°C . to permit of a conductivity value being obtained before precipitation of carbonate occurred. A series was obtained, however, from dilutions 50 to 8000; results are given below. The dilutions were with pure water, of conductivity 1.10×10^{-6} .

Conductivity. $\frac{1}{2}\text{Ca}(\text{HCO}_3)_2$.

V.	Uncorrected.	Corrected.
50	81.0	81.0
64	83.5	83.5
128	88.9	88.9
256	93.4	93.3
512	96.8	96.6
1024	100.0	99.6
2048	103.0	102.2
4096	106.7	(105.1)
8192	112.0	(108.7)
∞	—	108.0

As before, the values for the two highest dilutions show that hydrolysis is there appreciable. The value of the conductivity at infinite dilution may be taken as 108.0; taking the velocity of $\frac{1}{2}\text{Ca}^{+}$ 61.5, we have the velocity of the HCO_3^{-} ion equal to 46.5.

Finally, the conductivity of solutions of calcium sulphate, the values of which are also of importance in water analysis, was determined. (Compare Kohlrausch and Holborn, *Leitvermögen der Elektrolyte*, p. 161 (1898).) Calcium sulphate was precipitated by mixing dilute solutions of potassium sulphate and calcium chloride, filtered off from the solution, and thoroughly washed. A saturated solution at 25° C. was prepared by rotating a small quantity in a well-stoppered flask, half filled with water, in a thermostat for some days. The liquid was obtained free from excess of solid by means of a pipette fitted with a filter-cover; its concentration was determined gravimetrically by evaporating 100 c.c. carefully to dryness in a platinum basin. The water used for dilution had a specific conductivity of 1.20×10^{-6} , the whole of which is subtracted for correction, and the corrected results are as below. The figures are the mean of two determinations.

Conductivity. $\frac{1}{2}\text{CaSO}_4$.
(Saturated solution at 25° C. $v=32.50$.)

V.	Conductivity.
32.5	72.9
65	83.7
130	94.7
260	105.5
520	115.0
1040	123.3
2080	129.2
4160	134.1
8320	138.4

I desire, in conclusion, to express my thanks to Professor Walker, at whose suggestion the above investigations were carried out, for his advice and assistance during the progress of the research.

Chemistry Department,
University of Edinburgh.

XCVII. *The Composition of Two Simple Harmonic Motions exhibited by a Stretched String.* By A. I. STEVEN, M.A., B.Sc., Assistant Lecturer and Demonstrator in Physics, The University of Liverpool*.

[Plate XVI.]

THE compound character of a musical note emitted by a stringed instrument may readily be demonstrated by plucking the string, and then damping its motion at a convenient place, when only certain harmonics will still be heard. It is, however, rather difficult to exhibit this phenomenon to a large audience, and with a view to demonstrating the fact that a string can vibrate in different ways and in them all at one time, I have been led to devise the experiments described in this paper.

I propose to show how the composition of two Simple Harmonic motions of different periods and amplitudes may be exhibited (1) when the motions are in one plane, and (2) when they are in perpendicular planes.

I. *Two vibrations in the same plane.*

A light silk cord, 3 or 4 metres long, is stretched horizontally between two tuning forks A and B, electrically driven, and placed so that their directions of motion are vertical. The frequencies of the forks should be as low as possible, and in the ratio $a : b$ of the frequencies of the motions to be compounded. The apparatus having been so far arranged, proceed as follows:—Fix B in position and then set A vibrating. Adjust the tension by pulling A out or pushing it in till the string is set in stationary vibration of large amplitude with a loops in one plane. Unless the adjustment is very carefully made a circular motion of the string may be set up, which, of course, is not desired. Then let A be silenced and set B vibrating, when the number of loops visible should be b . Now set both forks vibrating, and each point on the string will execute a vibration which is the resultant of the two vibrations.

The character of the vibration of the string is more clearly seen with the aid of a stroboscopic wheel. The wheel should have *narrow* radial slits, and it is desirable that it should be controlled in such a manner that one slit passes any fixed point once during a vibration of the string when vibrating in one segment. (Professor Wilberforce's pattern

* Communicated by the Author.

of phonic wheel controlled by a tuning-fork is recommended.) If the wheel be running evenly at this rate, a person standing a few feet away and looking at the string through the slits as they pass will now see stationary a few waves of the compounded vibrations. If one fork only is sounding, he will see one of the components as a simple sine curve. Indeed, he will see a replica of the motion of the string as a whole, the effect being what would be produced by very greatly diminishing the length of the string without affecting its transverse motion. The explanation evidently is that all points of the string at any instant are in the same phase, and as the slit passes round, the part of the string viewed only differs from that previously seen by the phase having advanced a little in the time taken by the slit to pass round. In the same way, if the wheel go either too slowly or too quickly the motion will appear to progress in the backward or forward direction.

The figures 1 and 2 given on the plate (XVI.) are photographs through the stroboscope of the string in the case where the two tuning-forks are in the ratio 1 : 3. The lower fork had a frequency of 32 vibrations per second, and controlled the stroboscope, and that of the higher fork was approximately 96. The slight difference from the exact ratio gave rise to a continuous change of phase difference between the two vibrations, which was readily seen, as the curves gradually changed from the one form to the other. The photographs show the curves diminished to about one third of their apparent size. They represent :—

(1) The case when a trough of the wave motion of smaller period falls on a crest of that of larger period, and (2) when crest falls on crest. Though these photographs are exceedingly good they are more blurred than when the phenomena are observed. This is due partly to the difficulty of keeping the stroboscopic wheel in steady motion (for, of course, if it went for a short time either too quickly or too slowly, a displacement of the figure occurred), and partly to the varying phase difference, which made it necessary to expose the plate several times when the phase was approximately correct.

In order to make the phenomena visible to a large audience, I find that the stroboscopic wheel must be replaced by a rotating mirror. If a very narrow vertical beam of light from a lantern be allowed to fall on the string, and the image of the bright part of the string observed in the mirror, which is rotated about a vertical axis, it will trace out the time-displacement curve of a point on the

string. In illustrating a recent lecture the rotating wheel was driven electrically at constant speed. On starting one fork the usual sine curve was shown; on silencing it and starting the other, three waves for each of the former waves were made visible; and on starting the former again the compound vibration going through its various phases was exhibited.

The behaviour of the string when viewed without either of the aids above mentioned was in itself interesting. The amplitude was sufficiently large to enable one to see the string take the shape of the compounded wave, but as the phase difference between the two vibrations changed rapidly, the visual impression was of a three-peaked curve. One could see also that the phase difference gave rise to two apparent extra strings. The appearance was most marked at the places corresponding to the ventral segments of the string when giving three loops, and gradually disappeared towards the nodes where, of course, that vibration had diminished to zero amplitude. These two apparent strings coincided at the undisplaced position of the string when the view through the stroboscope was as in Pl. XVI. fig. 2, and travelled out to the edges of the loops, when the appearance was as in Pl. XVI. fig. 1. This is clearly to be explained by the fact that in the first case the place of slowest motion is when the string is in its undisplaced condition; and in the second, that then the place of slowest motion is when the string is most displaced.

Sometimes one of the vibrations set up by the tuning-forks took a circular form. In that case the centre of interest shifted from the view through the stroboscope to the motion of a point on the string as seen in the direction of its length. Such a point then exhibited a modified Lissajous' figure, corresponding to the composition of two vibrations in perpendicular planes in the ratio 3 : 1, with an extra vibration in one plane superposed. This brings me now to discuss

II. *The composition of two vibrations in perpendicular planes.*

For this it is only necessary to turn one of the forks through 90° , so that the direction of its vibration is horizontal and perpendicular to the string. In using this method, however, there is often a tendency to set up circular motions, and I find that it is much better if the two forks be set upright so that their directions of vibration are in the line of the string. There are at least two advantages in

adopting this longitudinal mode, for not only does the circular motion tend not to occur, but the fact that the number of loops in a given length of string under the same tension is now halved gives longer loops and larger amplitudes. The two vibrations seem always to set themselves at right angles, though there is no very apparent reason for such behaviour. It will be found advantageous not to attach the string at the tip of the prongs, but rather lower, as the effect of varying tension seems to hinder the two vibrations being maintained together if the amplitudes of the forks are too large. If the adjustments have been properly made, every point on the string will execute a Lissajous' figure. At any place which is a node for one vibration but not for the other the motion is in a straight line, and in passing through the node along the string a change of phase difference between the two vibrations of π occurs.

The two photographs Pl. XVI. figs. 3 and 4 exhibit exceedingly well the surface traced out by a brightly illuminated string executing such vibrations, and everyone will recognise two phases in the composition of vibrations in the ratio 1 : 3. The figure which stands out so distinctly is traced out by a point rendered specially brilliant by a piece of wax which was attached to the string. It can easily be seen that every little hair is carrying out a similar motion. The size of the pattern photographed was about 5 cm. in diameter, and it is possible to obtain them much larger. The phase difference in this case caused the figure to go quickly through all the forms usually figured in text-books. The effect of the relative amplitudes of the two vibrations at different points in the string was easily observed; where a node occurred for one vibration but not for the other, the motion was in a straight line; the change in phase in passing through a node turned the figure the opposite way.

It is obvious that any of Lissajous' figures may be obtained in this manner.

A case of some interest is that in which two vibrations with frequencies in the ratio 1 : 2 may be compounded by the use of a single fork. In the well-known experiments of Melde two positions of the fork only are considered: (1) The transverse mode, in which the period of the string is equal to that of the fork; and (2) the longitudinal mode, in which the period of the string is twice that of the fork. If the fork be rotated, so that the direction of its motion is inclined to the direction of the string, it is clear that two transverse vibrations whose frequencies are in the ratio 1 : 2 will be produced in it, and sometimes these set themselves at right

angles so that Lissajous' figures are obtainable. Pl. XVI. fig. 5 shows a loop of the string executing such a motion. The effect of varying relative amplitude of the vibrations can readily be traced in it. At the node of the transverse vibration the figure traced by a point on the string should be a straight line: in the photograph it appears as a curve with a convexity towards the fork; this is clearly due to the varying tension in the string caused by the large amplitude of the fork, the string having been attached in this case at the end of the prong. The curvatures of the figures at the ventral segments on either side of the nodal line are in opposite directions corresponding to the phase difference acquired in passing through it. Perhaps the most interesting form obtained by me in this way is that shown in Pl. XVI. fig. 6, which corresponds to a circular motion, with a simple harmonic motion of double its period, and more than double its amplitude superposed. The order in which the curve is traced is easily made out from the photograph.

To Professor Wilberforce are due my thanks for the great interest he has taken in these experiments.

George Holt Physics Laboratory,
The University of Liverpool.
1st March, 1912.

XCVIII. *The Relation between the Ranges of α Particles and the Periods of Transformation of Radioactive Bodies.* By Prof. H. A. WILSON, F.R.S., F.R.S.C., McGill University, Montreal*.

IT has been shown recently by Geiger and Nuttall† that there is an approximately linear relation between the logarithms of the transformation constants (λ) of radioactive substances and the logarithms of the ranges (d) of the α particles which they emit.

Radioactive transformations are somewhat analogous to monomolecular chemical reactions, but are atomic in character and independent of temperature. The kinetic energy of the α rays may be regarded as a measure of a quantity analogous to temperature which helps to determine the internal state of the atom. This quantity may be called the atomic temperature, and we may suppose that the rate

* Communicated by the Author.

† Phil. Mag. October 1911.

of decomposition of a radioactive substance depends on its atomic temperature in much the same way that the velocity of an ordinary chemical reaction depends on the ordinary temperature.

A somewhat similar rather loose analogy may be drawn between the emission of negative electrons by hot bodies and the emission of α rays. The higher the temperature the greater the velocity of emission, and the greater the number emitted in unit time.

If we suppose that the work necessary to be done by an α particle before it can escape from an atom is approximately the same for all radioactive atoms, then in view of the above considerations we might expect a formula of the type

$$\lambda = A\phi^{\frac{1}{2}}e^{-Q/2\phi} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

to be true. Here ϕ denotes the atomic temperature, Q the energy in calories required for the escape of one gram molecule of α particles, and A is a constant. The formula suggested is of the well-known type which represents the variation of the velocity of reactions and thermionic currents with temperature.

The mean kinetic energy of a molecule of a gas is equal to $\frac{3}{2}R\theta$, where R is the gas constant for one molecule and θ the absolute temperature. The range (d) of an α particle is equal to βv^3 , where β is a constant and v is its velocity. Hence we have

$$\frac{3}{2}R\phi = \frac{1}{2}mv^2 = \frac{1}{2}m\left(\frac{d}{\beta}\right)^{\frac{2}{3}},$$

or

$$\phi = \frac{m}{3R}\left(\frac{d}{\beta}\right)^{\frac{3}{2}}.$$

Substituting this in (1) we obtain

$$\lambda = B\left(\frac{d}{\beta}\right)^{\frac{1}{2}}e^{-3RQ/2m}\left(\frac{d}{\beta}\right)^{\frac{3}{2}},$$

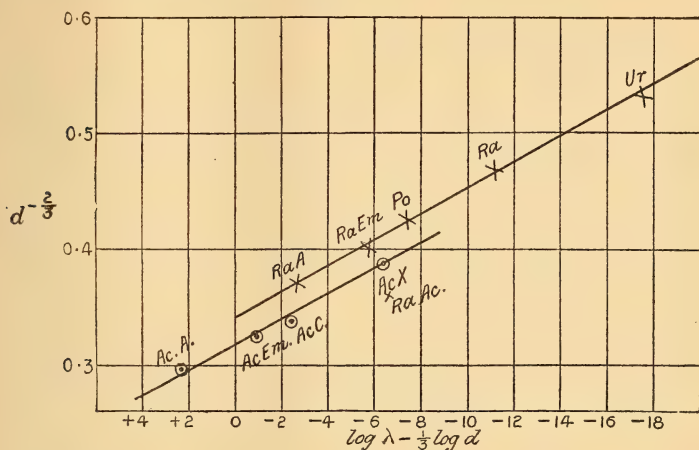
where B is a new constant. This equation gives

$$\log \lambda - \frac{1}{3} \log d = a + bd^{-\frac{2}{3}},$$

where $a = \log B - \frac{1}{3} \log \beta$ and $b = -3RQ\beta^{\frac{2}{3}}/2m$.

In the figure the values of $\log \lambda - \frac{1}{3} \log d$ are plotted against $d^{-\frac{2}{3}}$; and it appears that a nearly linear relation exists between these quantities in both series of radioactive bodies.

The values of λ and d were taken from the paper by Geiger and Nuttall (*loc. cit.*).



The equation (1) therefore represents approximately the relation between ϕ and λ ; so that the assumption that the energy necessary for an α particle to escape is the same in all cases appears to be approximately true.

The two lines are parallel, so that for both series of products b is the same, and the slope of the lines gives $b=205$.

$$\text{Hence } Q = -\frac{205 \times 2m}{3R\beta^{\frac{2}{3}}}.$$

For helium $m/R = 4/2 \times 4.2 \times 10^7$ and $\beta = 7.5 \times 10^{-28}$; so that $Q = 1.6 \times 10^{13}$ calories per gram molecule. The work for a gram molecule of electrons to escape from platinum is about 10^5 calories; so that the work for an α particle is about 10^8 times greater. The work for an electron to escape from platinum is about that necessary to separate two ionic charges (e) from a distance of 10^{-8} cm. or the radius of molecular action. The work for an α particle to escape is therefore about that required to separate two charges $2e$ from a distance of 10^{-16} cm.

We may say therefore that in the escape of electrons at high temperatures and in ordinary chemical actions electrons are separated from distances of the order of the radius of molecules, while in radioactive changes electrons are separated from distances about 10^8 times smaller.

XCIX. *Note on the Electron Theory of Thermoelectric Phenomena.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN the February number of the *Philosophical Magazine* Prof. O. W. Richardson has published a paper on "The Electron Theory of Contact Electromotive Force and Thermoelectricity." As his results with respect to the Peltier and Thomson effects are in disagreement with results I have obtained in a previous paper (N. Bohr, *Studier over Metalernes Elektrontheori*, Diss., Copenhagen, 1911), I shall be glad to be allowed to try to explain briefly the reasons for this disagreement.

Prof. Richardson uses a very interesting method to calculate the Peltier and Thomson effects. By this method, which is based upon deductions from the results of experiments on the emission and absorption of free electrons by hot metal-surfaces, electricity is imagined to be transferred by a reversible cyclic process through a circuit partly consisting of metals; and the amount of work gained and the heat absorbed by this process is discussed on thermodynamic principles. [It may be remarked that the process adopted for the calculation of the Thomson effect is not strictly reversible, and that the influence of this fact, as Boltzmann has shown (*Sitzungsber. d. Wiener Acad. d. Wiss., math.-nat. Kl.*, Bd. 96, Abt. ii. p. 1258, 1887; cf. my paper, p. 72), cannot be infinitely diminished by altering the dimensions and the shape of the piece of metal which forms the part of the circuit considered. We shall not, however, discuss this point further here.]

In the circuits considered by Prof. Richardson, the transfer of electricity through a piece of metal is established in the following way. Electricity in the form of free electrons is "condensed" from the surrounding space into the metal at one end of the piece of metal considered and allowed to "evaporate" from the metal at the other end. The Peltier and Thomson effects are then calculated from the difference between the whole amount of heat developed in the metal during the process considered and the amount of heat developed at the ends of the piece of metal by the condensation and evaporation of the electrons.

The latter quantity of heat is calculated from the difference in potential energy of an electron inside and outside the metal surface. This way of calculating is, however, in my opinion not justifiable, as the amount of heat developed at the

surface of the metal cannot be determined in such a simple manner. For the sake of brevity I shall consider here only the simple case in which the piece of metal is of uniform temperature and consists of two bars of different metals joined together, the condensation of electricity taking place in one and the evaporation in the other.

If an electric current flows through a metal there will be a transfer of energy through any surface in the interior of the metal as a consequence of the flow of electrons through it. The magnitude of energy transferred per unit of electric current will depend not only on the potential energy of the free electrons and on the temperature, but also on the conditions of motion of the electrons in the metal. For, in different metals according to the different conditions for the motions of the free electrons, the electric current will be distributed in a different way among the groups of electrons with the various absolute velocities.—If, for instance, we suppose that the electrons move freely between the metal molecules and are only affected by them by separate collisions, and if in these collisions the forces between the electrons and the molecules vary inversely as the n th power of their distance apart, the amount of kinetic energy transferred through a surface in the interior of the metal when a unit quantity of electricity is transferred through that surface will be $\frac{2n}{n-1} \cdot \frac{k}{e} T$ (*cf.* my paper, pp. 63 and 66), in which e is the charge on an electron, T the absolute temperature, and k the universal gas-constant referred to a molecule ($pv=kNT$).

The expression for the Peltier effect, calculated directly from the difference in the transfer of energy in the two metals, will therefore depend not only on (1) the difference in potential energy of the free electrons, but also on (2) the difference in kinetic energy transferred by the electric current in the two metals.—If, for instance, we suppose that the molecules in the one metal act upon the electrons as hard elastic spheres ($n=\infty$), and in the other as electric doublets ($n=3$, *cf.* my paper, p. 35), the part of the Peltier effect arising from (2) alone will be equal to $\frac{k}{e} T$, corresponding to a potential difference of c. 0.0235 volt, which is of the same order of magnitude as the greatest Peltier effect observed.

Now returning to Prof. Richardson's calculation, we see that in the determination of the heat absorbed or developed at the end of the piece of metal considered,

no regard is paid to the energy required for the establishment or extinction of the directed molecular flow of the electrons, which produces the transfer of energy in question. Hence, in Prof. Richardson's calculation of the Peltier effect—which he supposes to be quite general, *i. e.* independent of special assumptions about the forces between the molecules and the electrons—only the part of the effect which arises from a possible potential-difference between the two sides of the surface separating the two metals, is considered; the other part arising from a possible difference in the amount of kinetic energy transferred by the electric current in the two metals is not taken into account.

Quite similar considerations will hold for the Thomson effect.

It may finally be remarked that it can be shown that the calculated values for the thermoelectric constants when the above mentioned points are taken into account, will also satisfy—at least for a very general case—the conditions given by Lord Kelvin,—a result which does not seem to be rigorously deducible from thermodynamic principles (*cf.* my paper, pp. 71–75).

I am,

Yours faithfully,

N. BOHR.

Trinity College, Cambridge,
Feb. 5, 1912.

P.S.—Since the above was written another paper by Prof. Richardson has appeared (*Phil. Mag.* April 1912). In the fifth paragraph of this very interesting paper Prof. Richardson has generalized his calculation, no longer assuming that the potential energy of the free electrons inside the metal can be considered as constant. Quite similar remarks to those stated in the above note will, however, for exactly analogous reasons, hold for the relation between the results of Prof. Richardson's new calculation and those of my own calculations for the corresponding case.

C. Theory of Ionization by Collision.

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

I MUST protest that Professor Townsend has misunderstood me completely and that I did not make the statements which he attacks with such vigour. I was so far from accusing him of holding the "older view" of ionization that I suggested that he had dismissed it from consideration

rather too summarily. Nor have I attempted to support that view against that which he holds; I was careful to state that I did not wish to throw any doubt whatever on any of the physical assumptions which form the basis of his theory of ionization by collision.

My criticisms support rather than undermine that theory. I pointed out that, owing to a slip in his calculations, the formulæ which Professor Townsend employed to compare the results of his observations with the predictions of his theory were not an adequate expression of the assumptions on which that theory is professedly based; but that, when the error is removed, the observed and predicted values agree slightly better than before in the case of his own observations, and very much better in the case of my observations.

Prof. Townsend asserts with quite unnecessary severity that my remarks are either incorrect or unimportant. He has not doubted the correctness of this criticism, and I can hardly believe that he really regards it as unimportant that his theory should agree with observation.

I am,

Yours faithfully,

NORMAN R. CAMPBELL.

CI. *The Absorption of X-Rays and Fluorescent X-Ray Spectra.* By Professor C. G. BARKLA, M.A., D.Sc., and V. COLLIER, B.Sc., University of London, King's College*.

General Absorption Curves.

IN a paper on "The Absorption of Röntgen Rays"† Barkla and Sadler showed how the absorption by a given element of beams of homogeneous X-radiation varies with the general absorbability of the radiation employed. [The general absorbability may be measured in any substance whose spectral lines in X-rays are not within the range of absorbability and not near it on its more absorbable side. Aluminium is a convenient substance for all ranges usually dealt with, or even the much wider range covered by these experiments.] Curves showing the relation between the absorption in an element R say and in Al were given, and

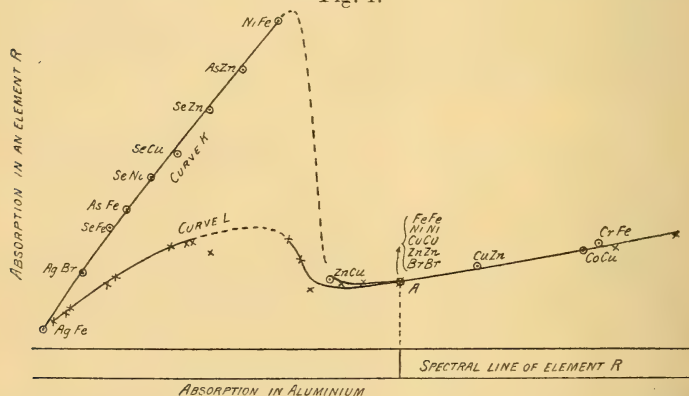
* Communicated by the Authors. The expenses of this research have been partially covered by a Government Grant through the Royal Society.

† Phil. Mag. May 1909, pp. 739-760.

the characteristics of the relation were seen to be the same whatever the element R employed. At that time, however, the series of spectral lines * had not been observed, nor had sufficient experiments been made to accurately test the generality of the curves over a large range of penetrating power, especially in the region of the spectral lines.

In further experiments † we have therefore examined the absorption of X-rays by Br and Ag, the latter of whose spectral lines of series K is about 35.5 times as penetrating as that characteristic of Fe. If we plot, as previously, absorption in Br or in Ag as ordinates, and absorption in Al of the corresponding homogeneous radiations as abscissæ, we get a curve possessing similar characteristics to those previously published for the absorbing elements Fe, Ni, Cu, and Zn. This was, of course, expected. If, however, we arrange the scales of ordinates and abscissæ for each

Fig. 1.



Showing relation between absorption in element R and in standard substance (Aluminium) in region of spectral line of R. One curve K is common to all elements R if spectral line is of series K. Curve L shows similar relation when spectral line is of series L.

absorbing substance such that the absorption of Fe radiation ‡ in Fe, Ni radiation in Ni, Cu radiation in Cu, &c., are all indicated by the one point A (fig. 1), it appears that there is

* Barkla, Phil. Mag. Sept. 1911, pp. 396-412.

† In this paper, as in the paper by Barkla and Sadler, the absorption coefficient λ is defined by the equation $I = I_0 e^{-\lambda x}$ in the usual notation. It should be noticed, however, that I represents the intensity of radiation of the same penetrating power as the incident radiation transmitted in the same direction as that of the incident radiation. It does not include the scattered or transformed radiations.

‡ (Series K.)

not only a similarity in general features, but that one absorption curve is common to all absorbing substances. The exactness of this in the case of absorption by Fe, Ni, Cu, Zn, and Br is remarkable, and is illustrated in fig. 1 by a few points obtained from experiments on absorption by each of these elements. Thus in fig. 1, curve K is seen to pass through points indicating absorption by Fe, Ni, Cu, Zn, and Br. In explanation of the notation it should be pointed out that the letters CuFe, for instance, denote absorption of Cu radiation by Fe. The points obtained from experiments on absorption by Ag do not fall exactly on the curve and have been omitted. There appears in this case to be a small displacement to the left. This might be caused by the one value AgAg being slightly too large. But quite apart from small possible errors of experiment, slight displacements to left or right are to be expected, as absorption in Al does not provide a perfect standard of reference—that is a perfect scale of abscissæ.

We thus see that for all these substances there is little or no variation in the shape of their absorption curves in the region of their spectral lines of series K. The connexion between the curve for a particular absorbing substance and the spectral line of that substance is shown in fig. 1, A being placed vertically above the spectral line shown in the lower portion of the figure.

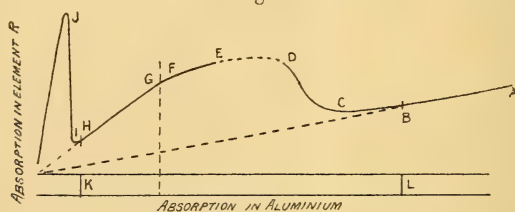
In order to investigate the shape of the absorption curve in the region of the spectral line of series L, experiments were made on the absorption of homogeneous beams of X-rays by Au and Pt. The spectral lines of series L for these elements is within the range of absorbability most easily experimented upon. The results are given in Table I. (p. 990). If now we compare the shape of the curves by arranging that the absorption of Au radiation (series L) in Au and of Pt radiation (series L) in Pt is coincident on the figure with the point A corresponding to Zn radiation (series K) in Zn, &c., we at once see a marked difference. Curve L (fig. 1) passes through points obtained by these experiments on Pt and Au. It possesses similar characteristics to curve K, but the ordinates are of very different magnitude. Thus the shape of the absorption curves in the region of a spectral line depends on the series to which the spectral line belongs and not to any appreciable extent upon the particular element in which the absorptions are made.

By a combination of the two curves K and L we get one absorption curve which is characteristic of every element

TABLE I.
Mass absorption coefficients $\left(\frac{\lambda}{\rho}\right)$.

RADIATOR.	ABSORBER.				
	C.	Al.	Ag.	Pt.	Au.
Zn	4.26	39.4	175	162.5	178.2
As	2.49	22.5	105.3	105.7	106.1
Se	2.04	18.9	87.5	92.1	102
Br	1.9	16.4	77.1	176	135.5
Rb	1.32	10.9	52.3	168	147
Sr	1.16	9.4	45.2	165	159.6
Mo	.81	4.7 [5.3]	26.5	103	111
Ag	.46	2.5	13.3	56.5	61.4
Sn	.35	1.57	16.5	47.1	51.7
Sb	.31	1.21	56.1		
I	.29	.92	46		
Ba	.26	.8	35.4		
Ce	.248	.6			

Fig. 2.



General absorption curve showing relation between absorption in element R and in standard substance (Aluminium). The connexion with the fluorescent X-ray spectrum is shown by the position of the spectral lines of R in the lower portion of figure.

hitherto experimented upon. Thus fig. 2 shows in the lower portion the fluorescent line spectrum of any element, horizontal distances from left to right representing instead of wave-lengths, absorbability in aluminium. Two definite absorbabilities have been found in the fluorescent X-radiation from a number of elements, the line of series L being roughly 300 times as absorbable as that of series K. As the

distance between the two lines on the spectrum is so great compared with the distance of one from the end, the scale of abscissæ has been made different in the two halves of the diagram separated by the broken line. The scale on the right-hand side has been reduced to about $\frac{1}{3\frac{1}{2}}$ that on the left. From many substances only the spectral line of series K has been observed, from others only that of series L, and from many light elements neither line, but there is strong evidence of the existence of both lines and indeed lines of other series not yet observed in the fluorescent spectra of many elements. There is no evidence that these lines do not exist in the fluorescent spectra of all elements. The curve shown above the characteristic spectrum of an element R, say, represents by its ordinates the relative absorptions in that particular element of the radiations whose absorbability in Al is represented by abscissæ. The ordinates to the right of the vertical broken line have been reduced in something like the same ratio as the abscissæ, though not accurately so, as from no single element has the complete absorption curve been obtained; consequently the true relative values of the ordinates in the two halves of the diagram have not been determined. In the case of some substances, the curve has been obtained in the region of the spectral line K only, in others in the region of line L, and in still others in regions far removed from the two.

We thus have, as far as is at present known, one fluorescent spectrum characteristic of all elements, the only difference between the various elements being that the scale of absorbability varies from element to element. Corresponding to this spectrum there is one absorption curve characteristic of all elements, the scale of absorptions (ordinates) varying with the element.

The character of this absorption curve for an element R, say, may be expressed as follows:—Commencing with rays of more absorbable type than the L line in the spectrum of R, the absorption in R is proportional to the absorption in the standard substance S. This is represented by the straight line AB, which being produced passes through the origin. As the radiation becomes more penetrating in type than the L line the absorption in R ceases to diminish at the same rate as in S, and then increases rapidly along CD. It then slowly approximates to proportionality with absorption in S, as shown by the line EF. Before the penetrating power of the K line is reached, the absorption in R becomes proportional to the absorption in S, as shown by the line GH. Again, when more penetrating rays than those of the K line

are used, the absorption in R rises above that of proportionality with S, and then rises rapidly as shown by IJ, the character of the rest of the curve being similar to that obtained on the more penetrating side of the L line, the features, however, being more strongly marked.

The similarity of the absorption curves may be mathematically expressed thus:—

$$\frac{x\lambda_R}{R\lambda_R} = f\left(\frac{x\lambda_S}{R\lambda_S}\right).$$

That is, the coefficient of absorption of any X-radiation in any element R divided by the coefficient of absorption of the radiation characteristic of R in R itself is a function of the coefficient of absorption of that X-radiation in S divided by the coefficient of absorption of the radiation characteristic of R in S,—the characteristic radiations being of the series K. This function is independent—or, at any rate, approximately independent—of the absorbing substance R for all substances hitherto experimented upon.

The relation between the absorption of a definite homogeneous X-radiation by various elements and the atomic weight of those absorbing elements has been indicated by one of us in a paper on “The Phenomena of X-ray Transmission”^{**}.

Observation of the similarity of the behaviour of all substances shows that it is possible to construct more accurately the curves showing the relation between these quantities.

Thus if we plot absorption $\left(\frac{\lambda}{\rho}\right)$ of a certain homogeneous

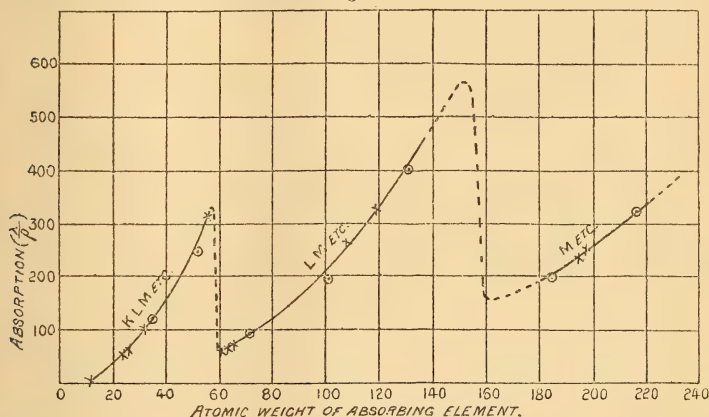
X-radiation—say Ni radiation of series K—by various elements, and the atomic weight of those elements, we have insufficient data to determine the shape of the curve in many regions. But by alteration of the scales of ordinates and abscissæ in similar curves got from experiments on homogeneous X-radiations of neighbouring penetrating power, we can build up a more accurate curve showing the relation. There is a slight variation in form between the curves obtained from experiments on radiations widely different in penetrating power, for the ratio of the atomic weights of the elements giving radiations of the same penetrating power (one in series K, the other in series L) is not a constant for all penetrating powers.

The curve shown in fig. 3 gives the relation between the absorption of Ni radiation (series K) by equal masses of

* Barkla, Proc. Camb. Phil. Soc. May 1909, pp. 257–268.

elements, and the atomic weight of these elements. The points obtained by experiments with the actual Ni-radiation are shown by crosses (x) and those by experiments on radiations of neighbouring penetrating power by circles (○).

Fig. 3.



Showing absorption of a homogeneous X-radiation by equal masses of various elements. The particular radiation used is characteristic of elements of atomic weight 61.3 and 160 approximately (series K and L respectively). For more penetrating radiations the maxima and minima are further to the right: for more absorbable radiations they are to the left.

It may be observed that the absorption increases with the atomic weight of the absorbing substance, as long as the fluorescent X-radiations of the same series are intensely excited in the absorbing substance. When, however, the atomic weight of the absorbing element becomes so high and its fluorescent radiation of either series K or series L so penetrating that it is not excited (or is only slightly excited) by the radiation used, then the absorption suddenly drops. We thus get a general rise of absorption with atomic weight of the absorbing substance, with sudden drops within a much narrower region of atomic weights. The letters L, M, N, &c. indicate the spectral lines emitted under exposure to the particular radiation dealt with. These explain the rise and fall in the curve. Thus, the particular radiation used (Ni radiation of series K) is capable of exciting in elements of lower atomic weight than 61.3 the radiations of series K, L, M, &c. In elements of atomic weight from 61.3 to about 160, it excites radiations of series L, M, &c., but not of series K. Less energy of the particular primary radiation is thus absorbed than would have been the case if K radiation had been excited. Again, in elements of higher atomic

weight than 160, neither the K nor the L radiation is excited, and again the absorption is less than what it would have been if these radiations had been excited.

Similar curves may be obtained by using any homogeneous X-radiation, but if the radiation is of more penetrating type, all the maxima and minima are displaced to the right, and if more absorbable to the left.

Absorption in Elements of Low Atomic Weight.

The absorption by light elements is interesting, because when penetrating rays are transmitted through them by far the greater proportion of the radiation is merely scattered, and if surrounded by light elements rescattered. It has been shown by one of us that the energy of Röntgen radiation lost by scattering during transmission through a thickness dx of a light element is given by the expression

$$dE = -sE dx,$$

where s is a constant for rays of all penetrating powers, and is proportional simply to the density of the light scattering substance. Thus, if $\frac{\lambda}{\rho}$ is the mass-absorption coefficient, we may by analogy call $\frac{s}{\rho}$ the mass-scattering coefficient.

This is constant for all matter made up of light atoms. The lightest elements absorb much less than heavier ones, mass for mass, so that $\frac{\lambda}{\rho}$ diminishes with the atomic weight of the absorbing element. It also diminishes as the penetrating power of the radiation increases. As $\frac{s}{\rho}$ remains constant, $\frac{s/\rho}{\lambda/\rho}$ or $\frac{s}{\lambda}$ (which is the fraction of the absorption coefficient due to scattering) becomes great when penetrating rays are passed through light elements.

Now, as the penetrating power of a radiation varies, the absorptions in any two substances remain approximately proportional, provided the range of penetrating power experimented upon does not include or approach on the more penetrating side the penetrating power of a fluorescent radiation characteristic of either A or B. If we may be allowed, for the sake of simplicity, to express this in the terms applied to light, it may be stated thus:—The absorptions of X-rays in two substances A and B bear an approximately constant ratio one to the other over a range of wave-lengths not including a spectral line of either and not near to a spectral line of either on the side of shorter wave-lengths. As the scattering is independent of the wave-length, we should expect this law to cease to hold when the loss by scattering is an appreciable

fraction of the total loss. By experimenting on the absorption of radiations of high penetrating power by elements of low atomic weight, this may be tested. In Table II., column 2, are given the ratios of absorption in carbon to absorption in aluminium of various homogeneous X-radiations. The value rises from .1 to .4. If, however, the scattering coefficient $\frac{s}{\rho}$ be subtracted from each absorption coefficient, as given in Table I., we find that the ratio of absorptions is again constant, as shown in column 3.

$[\frac{s}{\rho}$ has been previously shown to be .2.]

Thus to obtain perfect generality in the absorption laws it is necessary to neglect (or subtract from the total absorption as defined above) the absorption due to scattering. This becomes the most important term in the absorption of penetrating radiations by light elements, something like 80 per cent. of Ba radiation (series K), for instance, being scattered by carbon. A larger proportion is, of course, scattered by elements of still lower atomic weight.

TABLE II.

Radiation: the fluorescent X-radiation, series K, from elements below.	Ratio of absorption in carbon to absorption in aluminium [absorption includes radiation scattered].	Ratio of absorption in carbon to absorption in aluminium [absorption does not include radiation scattered].
	$\frac{(\lambda/\rho)_C}{(\lambda/\rho)_{Al}}$	$\left(\frac{\lambda-s}{\rho}\right)_C \div \left(\frac{\lambda-s}{\rho}\right)_{Al}$
Cr	.112	.111
Fe	.114	.112
Co	.111	.108
Ni	.111	.108
Cu	.109	.105
Zn	.108	.104
As	.111	.103
Se	.108	.99
Ag	.164	.104
Sn	.223	.109
I	.315	.125
Ba	.325	.10
Ce	.413	.12
	} approximate.	} approximate.

Absorption in Gases and Vapours.

No systematic experiments have previously been made on the absorption of homogeneous beams of X-rays by gases. There appears, however, to be no doubt as to the generality of the absorption laws, whether applied to solids, liquids, or

gases. The work of Benoist with heterogeneous beams showed that, and since his time hundreds of experiments have only shown that X-ray phenomena are independent of the physical state of the substance concerned. It is, however, necessary in many investigations to know the magnitude of the absorption of homogeneous X-radiations by substances which are usually in the gaseous state, and which were not dealt with by Barkla and Sadler.

Experiments were made on the absorption by air at various pressures. The absorption was found to be proportional to the pressure within small errors of experiment. The absorption of the more penetrating rays was too small to be determined experimentally by the method used, but the absorption of the fluorescent radiations (series K) from copper and zinc were found as below. Knowing the absorption of the homogeneous radiations in aluminium and the absorption of these two particular radiations in air, by the law of proportionality of absorption (after elimination of that portion due to scattering) the absorption in air of many radiations was calculated *. Thus, using the notation as before, $\frac{(\lambda' - s') \text{ in air}}{(\lambda - s) \text{ in Al}}$ is constant.

In determining the absorption coefficients for any other gas, the ionization in an electroscope was observed first with air in the absorbing chamber in the path of the beam and subsequently with the particular gas in that absorbing chamber. Then

$$I_g = I_a e^{-(\lambda_g - \lambda_a)x},$$

where λ_a and λ_g are the coefficients of absorption in air and in the gas, x the length of the path through the absorbing gas, I_g and I_a the intensities as measured by the ionization after traversing the gas and air respectively. The only unknown was λ_g .

In the experiments on vapours, the absorption by a mixture of air and vapour at known partial pressures was determined and a correction was subsequently made for the absorption by the air present. The results are given below (Table III.). The values given in italics were obtained by interpolation.

From these results it may be observed that the laws of absorption are the same for gases as for solids :—

The absorptions in two gases A and B bear an approximately constant ratio one to the other through a range of absorbability not including a spectral line of either A or B, and not approaching one of these spectral lines on the more penetrating side.

* Sadler has experimentally determined λ in air for As radiation. The agreement with the value given is very close.

TABLE III.—*Absorption Coefficients (λ).*

Radiation: the homogeneous fluorescent radiation (series K) from elements below.	Air (76 cm. & 0° C.).	SH ₂ (76 cm. & 0° C.).	SO ₂ (76 cm. & 0° C.).	C ₂ H ₅ Br (16·6 cm. & 0° C.).	CH ₃ I (13·5 cm. & 0° C.).
Fe	·0202	·204	·24	·112	·384
Co	·0165	·181	·20	·089	
Ni	·0136	·149	·166	·071	·319
Cu	·0109	·121	·134	·057	·273
Zn	·0090	·104	·112	·047	·225
As	·0053	·06	·066	·028	·132
Se	·0044	·049	·0546	·024	·11
Br	·0039	·044	·050	·021	·098
Sr	·0023	·0248	·0281	·071	·060
Mo	·00127	·0137	·0160	·046	·035
Ag	·00077	·0060	·0079	·0236	·020

As the rays absorbed become more penetrating (as measured by any substance whose spectral lines are far removed) than a spectral line of A or B, the absorption in that particular substance rises in the manner shown in fig. 1, and ultimately approximates to proportionality again for radiations far removed from the spectral line.

It may be remarked, too, that the absorption in SO₂ is as much greater than in SH₂ as may be expected from the law that the total absorption is the sum of the atomic absorptions. From the most accurate experiments on the absorption by SO₂ and SH₂ it is evident that the absorption in oxygen is about 1·3 times that in air (neglecting the absorption due to scattering). The absorption by hydrogen is neglected. This result is interesting from the fact that the ionizations in the gases SO₂ and SH₂ are in the reverse order of magnitude*.

Summary.

Continuing the work of Barkla and Sadler, the absorption of radiations whose penetrating power is close to that of the spectral lines of the absorbing substances has been investigated in detail.

The relation between the absorption in an element R and the absorption measured in a substance whose spectral lines are far removed is found to be practically identical for all substances experimented upon.

One curve is drawn showing the relation for all substances.

The relations in the neighbourhood of spectral lines of series K and series L are, however, widely different.

The absorptions in various gases and vapours have been determined and the generality of the laws further verified.

* Barkla and Simons, Phil. Mag. Feb. 1912, pp. 317-333.

CII. *Anisotropic Expansion of a Drawn Tube of Vitreous Silica.* By H. L. CALLENDAR, M.A., LL.D., F.R.S.*

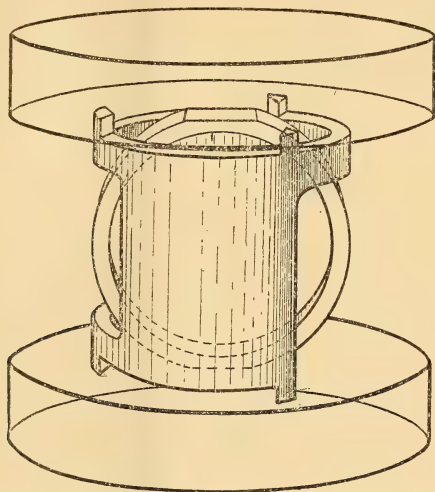
IT has been customary to assume that the expansion of an amorphous material should be isotropic, and the cubical coefficient has generally been taken as three times the linear. The discrepancy between the value of the cubical coefficient of silica from 0° to 100° C., namely 1.00×10^{-6} (deduced from the weight thermometer observations of Harlow and Eumorfopoulos by assuming the values of Callendar and Moss for the absolute expansion of mercury), and the values of the linear coefficient [$.500 \times 10^{-6}$ (Chappuis), $.465 \times 10^{-6}$ (Scheel), $.424 \times 10^{-6}$ (Randall)], has not unnaturally been regarded by Scheel and Heuse (Phil. Mag. March 1912, p. 412), and also by Eumorfopoulos (Phil. Mag. April, 1912, p. 653) as conclusive evidence of an error in the determinations of Callendar and Moss. The magnitude of the error in the cubical coefficient would vary from $.50 \times 10^{-6}$ to $.27 \times 10^{-6}$, according to the value selected for the linear coefficient.

Considering the great care taken in the testing and verification of the apparatus for the absolute expansion of mercury, and the close agreement of the observations taken before and after the whole apparatus had been dismantled and set up afresh with new tubes, it seemed to me scarcely possible that an error of this order of magnitude should exist in the results. In the April number of the Philosophical Magazine, p. 682, I, therefore, expressed the opinion, "that the explanation must be sought in the inequality of axial and radial expansion of a drawn tube due to intrinsic strain." In order to settle the question, if possible, by a direct appeal to experiment, I obtained from the Silica Syndicate of Hatton Garden, who had supplied the bulbs employed by Harlow and Eumorfopoulos, a drawn silica tube, 2 cm. in diameter, as nearly as possible similar to those from which the bulbs had been made. A tripod and a ring were cut from this tube by Messrs. Hilger, and were arranged as shown in the annexed figure for observing the difference of the axial and radial expansion by the Fizeau method. The design was exhibited and described at a meeting of the Physical Society on April 26th, but I was unable to give the results of the test at the time, as the worked specimens did not arrive until a day or two after the meeting.

With the assistance of Mr. A. Eagle, I have since succeeded in obtaining several concordant determinations of the difference between the axial and radial coefficients of expansion of this particular tube. The exact reduction of the

* Communicated by the Author.

results depends to a slight extent on the value assumed for the expansion of the 2 cm. tripod, which has not yet been



completely determined. It is possible, however, to state that the axial coefficient exceeds the radial by $\cdot 20 \times 10^{-6}$ over the range 0° to 100° C. Assuming the value $\cdot 465 \times 10^{-6}$ (the mean of the results above quoted for the linear coefficient) as being the value of the axial coefficient of the tripod, it is clear that the cubical coefficient would come out $\cdot 995 \times 10^{-6}$, which agrees as closely as could be expected with the result deduced by Harlow and Eumorfopoulos independently assuming the values of Callendar and Moss for the absolute expansion of mercury.

It may be objected that, although the axial and radial coefficients differ, the mean of the three must agree with the value for an isotropic specimen. Taking Chappuis' value $\cdot 50 \times 10^{-6}$ as representing an isotropic specimen, the axial coefficient of the tripod would have to be $\cdot 63 \times 10^{-6}$. In view of this objection, the axial coefficient of the ring, which is probably the same as that of the tripod, was measured on three days, and found to be $\cdot 455 \times 10^{-6}$; but no great stress is laid on this result (further than as confirming the value above assumed) because the ring is only 6.5 mm. wide, and was not intended for this determination.

The principal objection advanced by Eumorfopoulos against the results of Callendar and Moss at low temperatures, where the observations are admittedly more difficult, appears to be that, according to his weight thermometer, the cubical expansion of silica would vanish between 0° and 15° C. This apparently impossible result is confirmed by the observations

with the ring and tripod, which show that the difference between the axial and radial coefficients increases, while the axial coefficient diminishes more rapidly at low temperatures.

I have also investigated the expansion of a drawn silica rod, 30 cm. long, by a Newton's ring method, giving one whole ring for 10^{-6} expansion. The results will be published by the Physical Society, and are of interest as confirming the importance of the effects of strain.

CIII. *Notices respecting New Books.*

Physical and Chemical Constants and some Mathematical Functions.

By Dr. G. W. C. KAYE and Professor T. H. LABY. Pp. vi + 153. Longmans, Green & Co. Price 4s. 6d. net.

IT is not often that we would turn to a collection of data for stimulus; but there is something decidedly invigorating about this new collection of physical and chemical constants. The authors have evidently set before themselves the aim of making use of the large amount of work of precision which has been done in recent times and of discarding much that was becoming out of date. From the point of view of general interest they have had the advantage of the rapidly increasing amount of perfectly new matter in connexion with radioactivity and ionization, and especially of those data which apply particularly to the atom or molecule. The presence of these, collected for the first time in one volume, enhances the interest of the book. It gives one in summary form an idea of the great achievements effected by modern workers in science.

The book must, however, be considered chiefly in regard to its utility. The present writer, since the volume appeared, has used it at every possible opportunity with the object of estimating its utilitarian value. In making this estimate it must be remembered that it does not attempt, as Landolt and Börnstein's tables do, to give practically every datum of value. This would, of course, be impossible in a work of its modest size and insignificant price. The worker who wishes some guide as to what has been ascertained on a particular subject may therefore go away disappointed. The object clearly has been to include as many as possible of those data which are constantly required in connexion with research or teaching work; and the success is very great. There is no question that the authors will soon find their book in every physical and chemical laboratory; there is no other that comes anywhere near it in utility.

This being the case, it behoves us to point out a few particulars in which improvement may perhaps be effected.

On p. 5, the value of the gas constant R should be specified as ergs per gram molecule, not per gram. The electrical and magnetic definitions (pp. 5 & 6) require in some cases the specification of the medium (air or vacuum). The definition of specific

FIG. 1.—DIAGRAM
PHOTOGRAPH

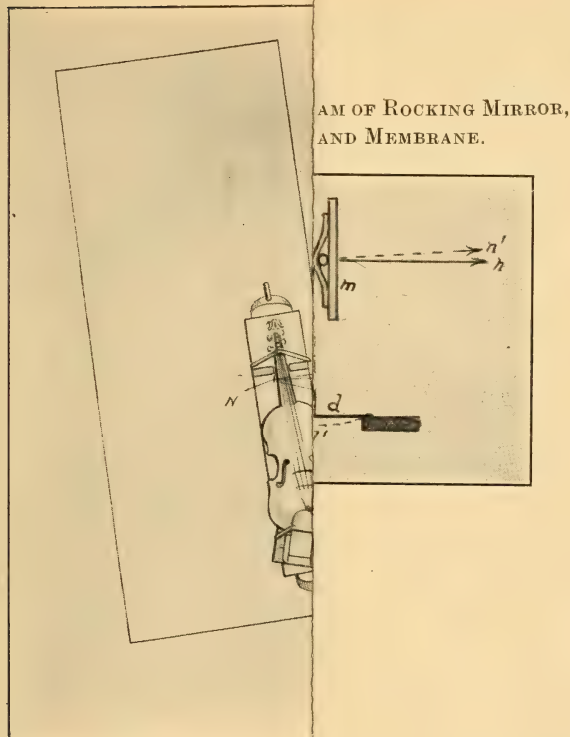


DIAGRAM OF ROCKING MIRROR,
AND MEMBRANE.

MIRROR MOUNTED ON BELLY.

FIG.
V

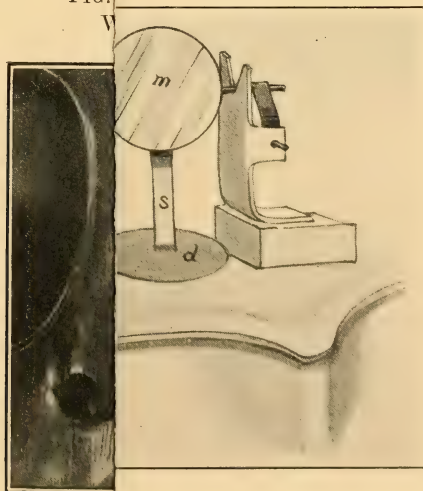


FIG. 1.—DIAGRAMMATIC PLAN OF EXPERIMENTAL ARRANGEMENTS FOR PHOTOGRAPHING VIBRATIONS OF VIOLIN STRINGS AND AIR.

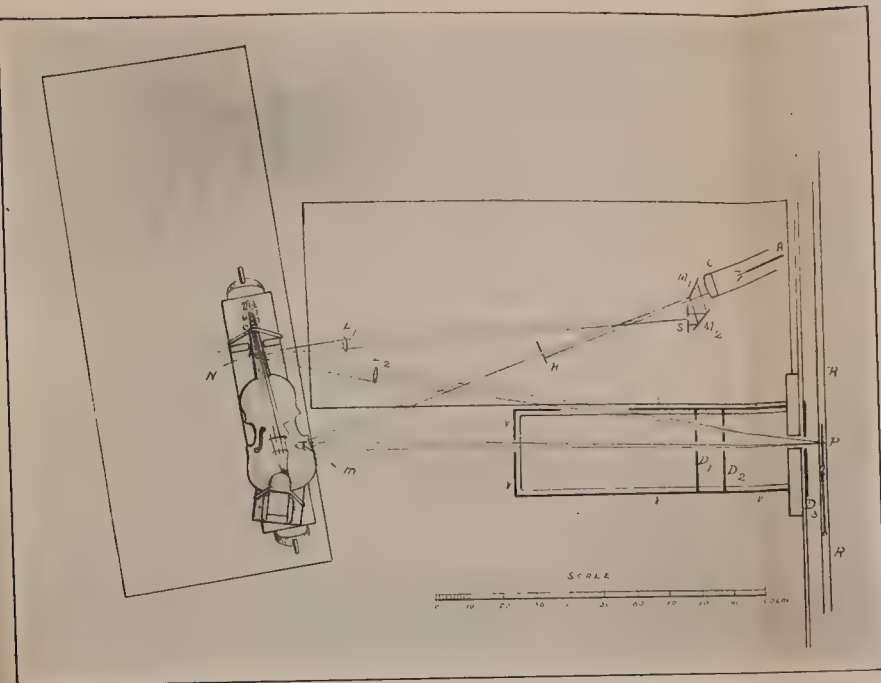


FIG. 2.—RIGHT SOUND HOLE COVERED WITH WHITE PAPER AND DARK MEMBRANE.

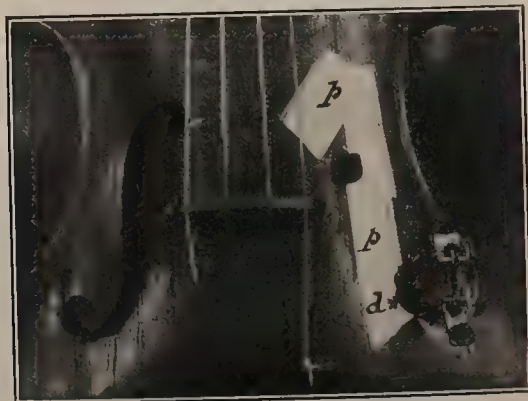


FIG. 3.—DIAGRAM OF ROCKING MIRROR, STALK AND MEMBRANE.

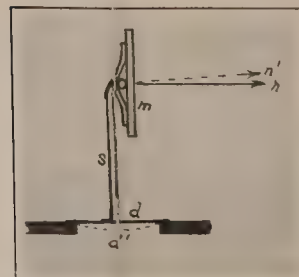
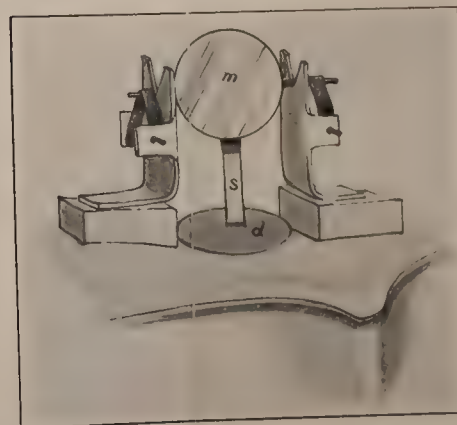
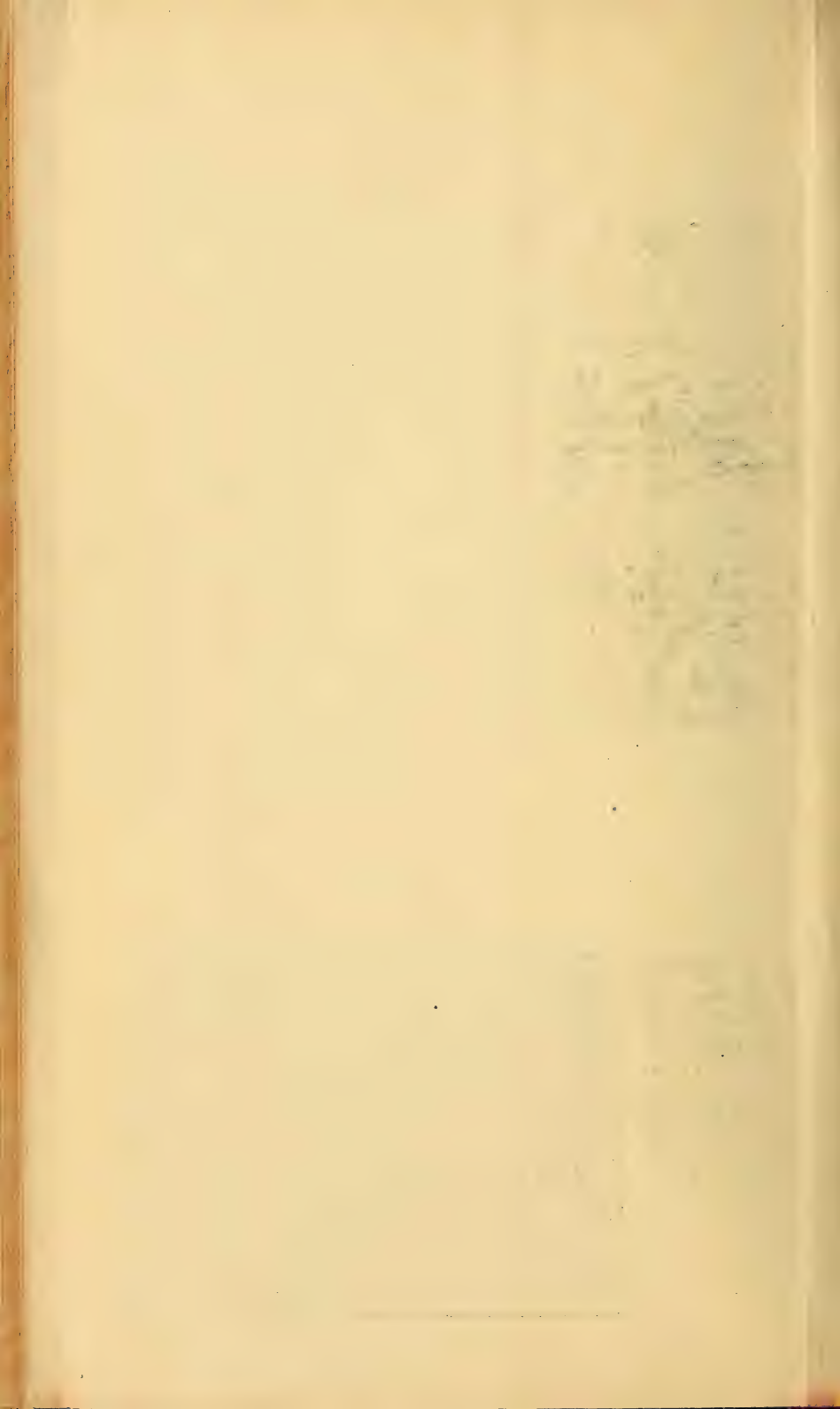


FIG. 4.—ROCKING MIRROR MOUNTED ON BELLY.

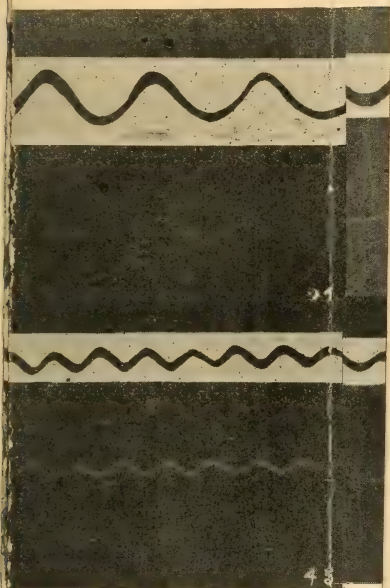




D-string plucked at $\frac{1}{4}$.

9

D-s



20

E-string plucked at $\frac{1}{4}$.

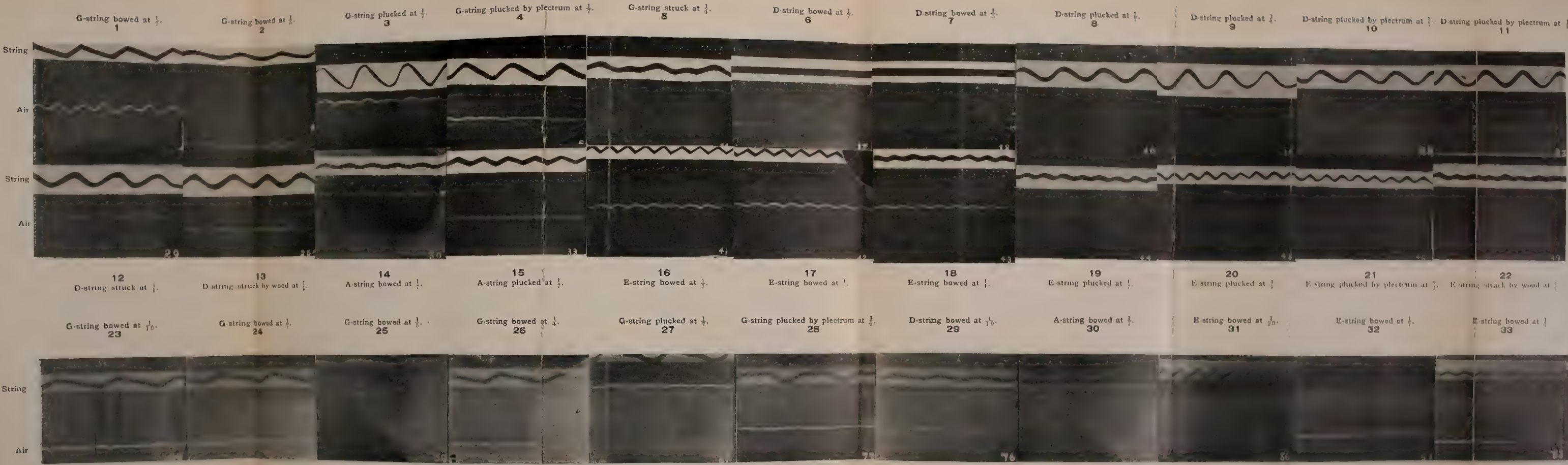
E

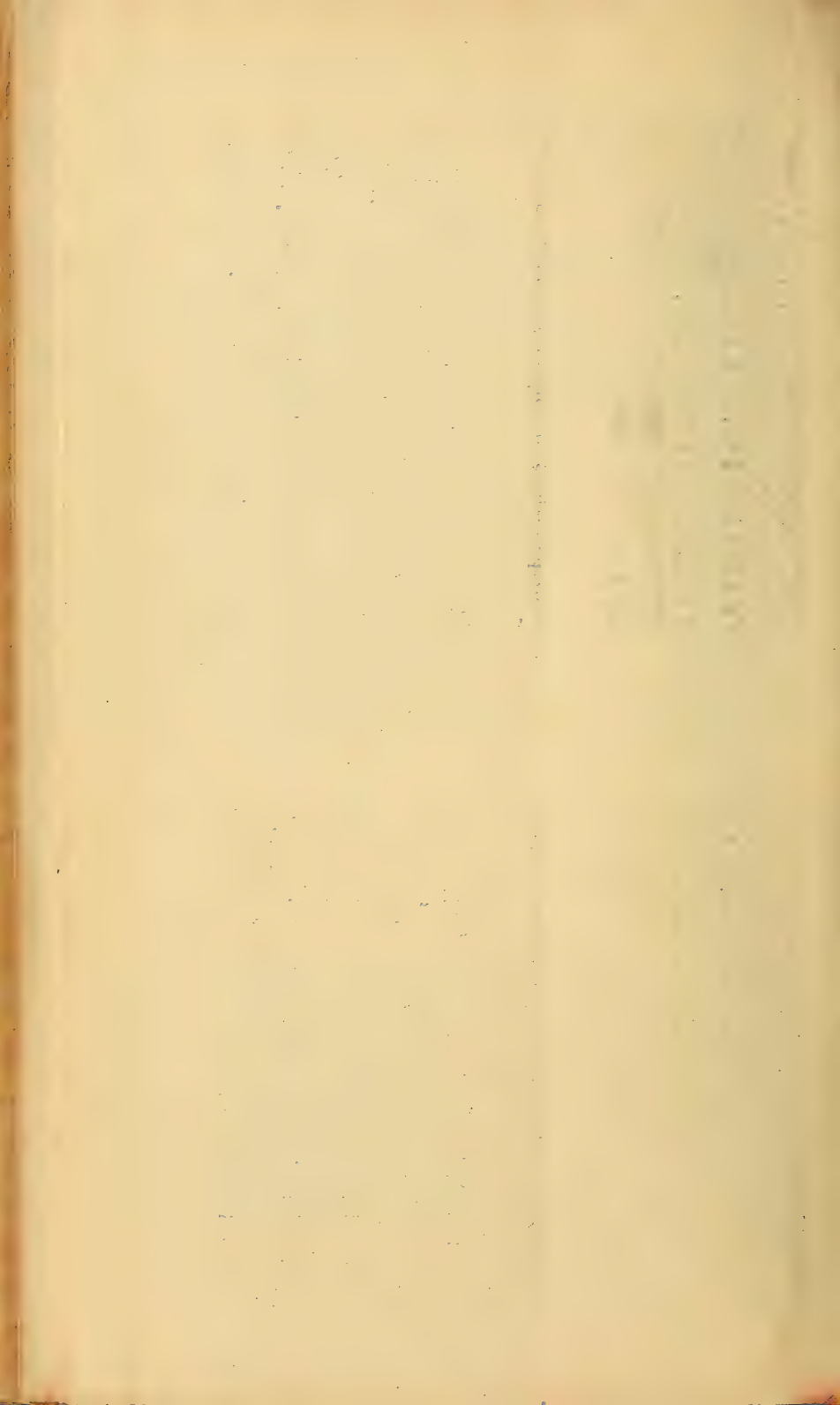
E-string bowed at $\frac{1}{20}$.

31



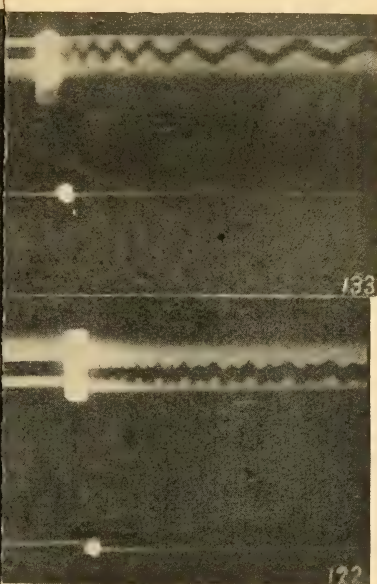
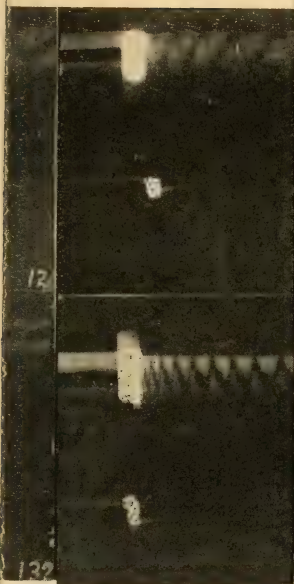
PHOTOGRAPHS TAKEN UNDER ORDINARY
CONDITIONS OF SHOOTING PLATES.
CLAMP MOUNTING OF MIRROR.
Belly Mounting of Mirror.





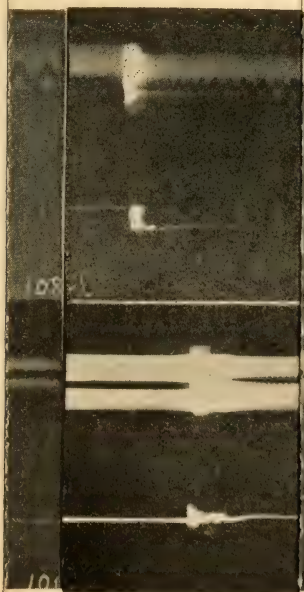
G-string plucked
37

G-string struck at $\frac{1}{7}$.
40



at $\frac{1}{4}$.
D-string plucked
44
A-string plucked by
51

47
D-string struck by wood at $\frac{1}{7}$.
A-string struck by wood at $\frac{1}{4}$.
54



at $\frac{1}{7}$.
E-string plucked by
58

61
E-string struck by wood at $\frac{1}{4}$.

PHOTOGRAPHS TAKEN UNDER SPECIAL CONDITIONS OF SHOOTING PLATES TO SHOW INITIAL MOTIONS.

BARTON & KILBY.

Phil. Mag. Ser. 6, Vol. 23, Pl. XV.

G-string bowed at $\frac{1}{7}$.
34

G-string bowed at $\frac{1}{7}$.
35

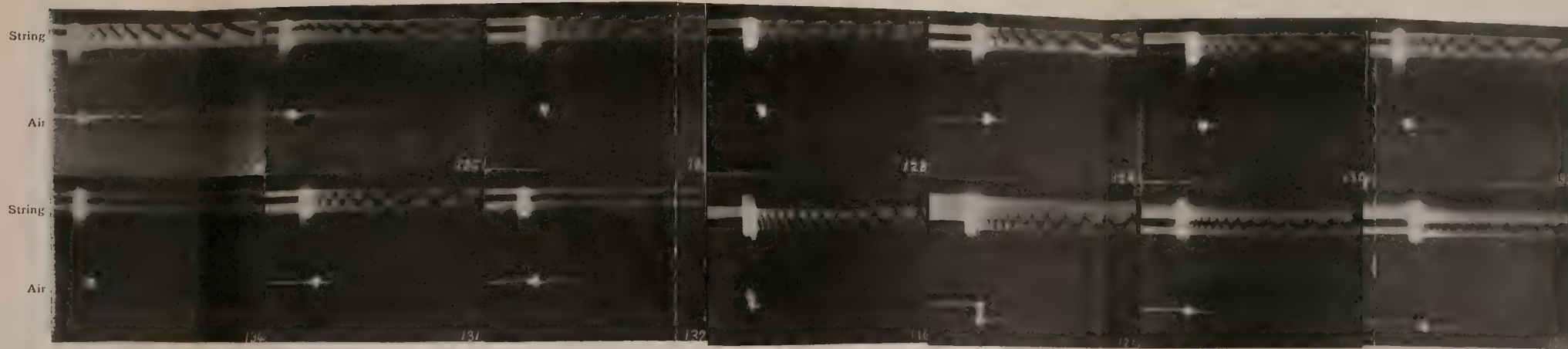
G-string plucked at $\frac{1}{7}$.
36

G-string plucked at $\frac{1}{7}$.
37

G-string struck by plectrum at $\frac{1}{7}$.
38

G-string plucked by plectrum at $\frac{1}{7}$.
39

G-string struck at $\frac{1}{7}$.
40



G-string struck at $\frac{1}{7}$.
41
A-string bowed at $\frac{1}{7}$.
48

G-string struck by wood at $\frac{1}{7}$.
42
A-string plucked at $\frac{1}{7}$.
49

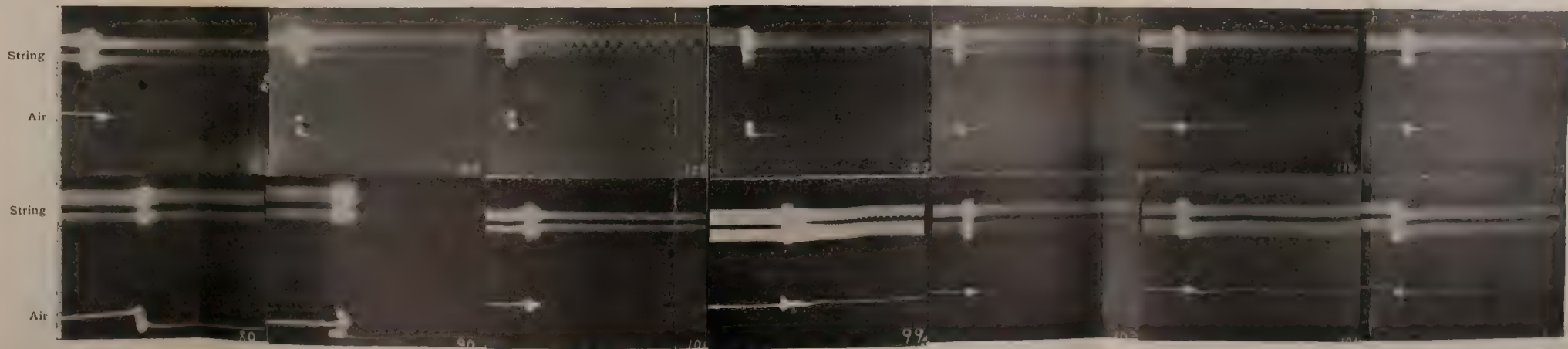
G-string struck by wood at $\frac{1}{7}$.
43
A-string plucked at $\frac{1}{7}$.
50

D-string plucked at $\frac{1}{7}$.
44
A-string plucked by plectrum at $\frac{1}{7}$.
51

D-string plucked by plectrum at $\frac{1}{7}$.
45
A-string plucked by plectrum at $\frac{1}{7}$.
52

D-string struck at $\frac{1}{7}$.
46
A-string struck at $\frac{1}{7}$.
53

D-string struck by wood at $\frac{1}{7}$.
47
A-string struck by wood at $\frac{1}{7}$.
54



E-string plucked at $\frac{1}{7}$.
55

E-string plucked at $\frac{1}{7}$.
56

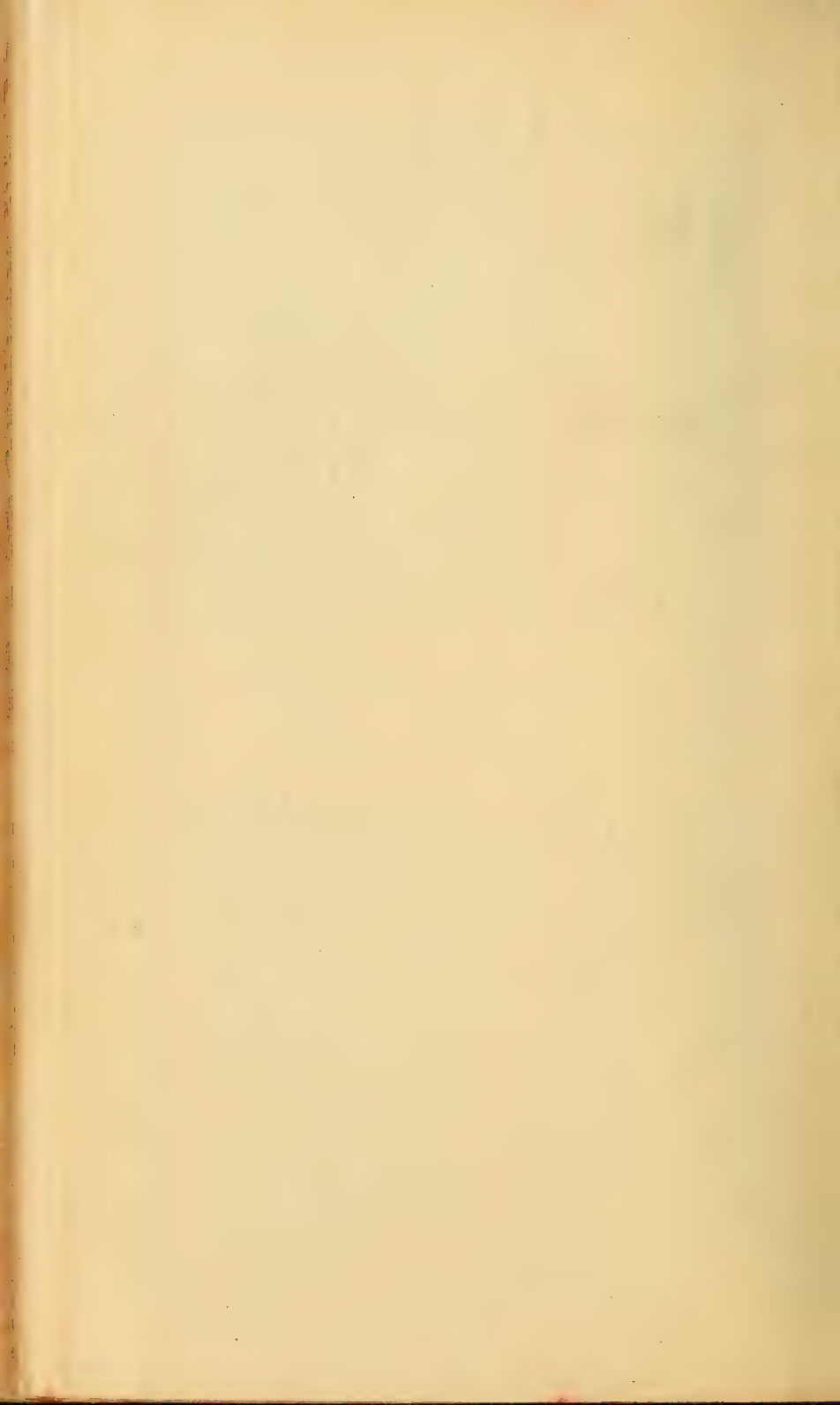
E-string plucked by plectrum at $\frac{1}{7}$.
57

E-string plucked by plectrum at $\frac{1}{7}$.
58

E-string struck at $\frac{1}{7}$.
59

E-string struck at $\frac{1}{7}$.
60

E-string struck by wood at $\frac{1}{7}$.
61



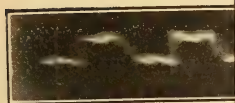


FIG. 6.

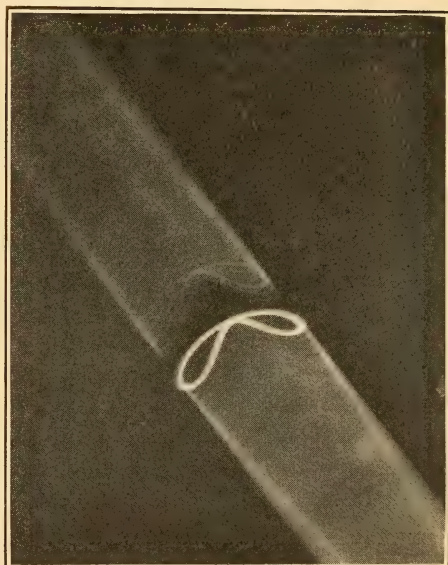


FIG. 1.



FIG. 2.



FIG. 3.



FIG. 4.



FIG. 5.

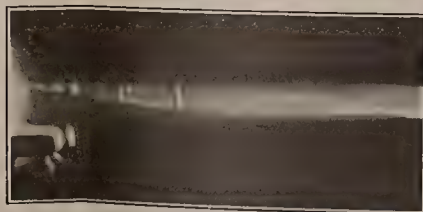
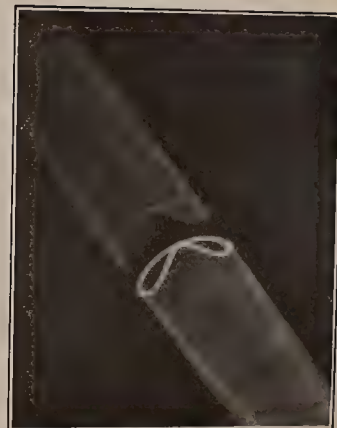
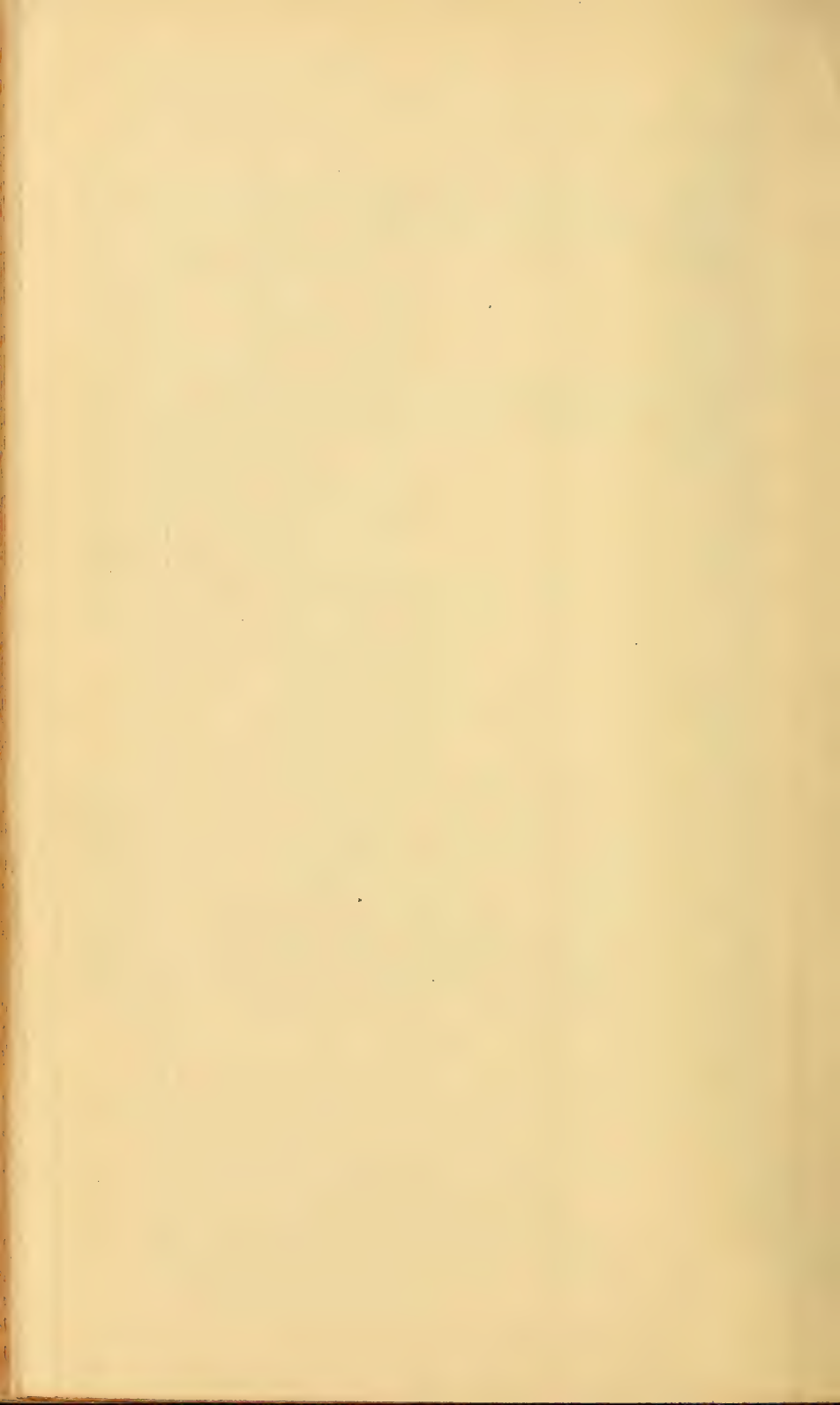


FIG. 6.





resistance as resistance per unit area per unit length is surely open to criticism, although worse definitions have been given. The terms self and mutual inductance require recognition. On p. 10, Benoit requires the accent. In the writer's opinion the critical volume (p. 34) can have only one meaning, and it is not the meaning for which the data are given here; he latter are not of much direct use; and since they are exactly three times the value of b given on the same page, they could easily be calculated by those who may require them. On p. 35, Loschmidt is wrongly spelt. The formula given on p. 50 for the boiling-point expresses the *change* in boiling-point.

On p. 39 the table of bursting strengths of glass tubing seems very inadequate even allowing for the recommended factor two. The numbers given no doubt correspond to the values obtained from a simple theory; but in practice a very much greater factor of safety than two is required. The table as it stands is only an encouragement to disaster. In the value for $\log p$ of mercury vapour on p. 41 a decimal point is wanted. The approximate formula of Callendar and Moss for the expansion coefficient of mercury between 0° and 200° C. is stated on p. 55 to be correct to 1 in 2000; at 0° itself it is in error by 5 parts in 1800. In the formulæ for the latent heat of water (p. 60) H. N. Davis' value based on 37 available values should be given in a future edition; this formula is $L_t = 92.93(365 - t)^{.3150}$. On p. 65, Lummer is wrongly spelt. The word 'cathion' depends upon a mistaken etymology; we thought it was being purged from scientific literature. The symbol N is used in two senses in the formula near the top of page 98; in one case probably N_m was intended. On p. 106 the line beginning with the symbol $a\theta$ requires revising; the numerical value given is that of a ; the statement under the heading 'definition' should be Energy of a gas molecule at $\theta^\circ\text{C.} = a\theta = 3p/2N$ or $a = 2.02 \times 10^{-16}$ ergs per deg. per gr. mol. R is expressed in ergs per gr. mol. and in litres atm./gr. mol., not per gram.

The triviality of most of these corrections sufficiently indicates the great care that has been expended in reading the proofs. The authors are to be congratulated on their work.

The mathematical tables include the values of e^{-x} , four-figure logarithms from 100-1000 (with table of proportional parts), corresponding antilogarithms, five-figure logarithms from 100-1000 and proportional parts, and four-figure tables of squares, reciprocals, sines, cosines, tangents, and radians. We have used some of these tables. The plan of putting a vertical line on each side of the '5' column we have found to be a most excellent one. The five-figure table fills two pages; but they are arranged so that no turning over is necessary.

The index is an excellent one.

The binding is a limp cloth which has a habit of curling up when the book is left on the table. A stiff strong binding is much more suitable for a book of this kind.

INDEX TO VOL. XXIII.

- ABERRATION**, on changes in diffraction spectra produced by, and on the, of an echelon grating, 25.
- Absorption**, on selective, by resonating gas molecules, 689.
- problems in radioactivity, on, 242.
- spectra and the solvate theory of solution, on, 730.
- Accumulator plates**, on the unilateral conductivity of sulphated, 742.
- Æther disturbance**, on the propagation of periodic, 809.
- Air**, on the charges on thermions produced in, 173; on the absorption of Röntgen rays in, 683; on the production of condensation nuclei in, by intense cooling and by ultraviolet light, 849.
- Alkaline earths**, on the positive thermions from the salts of the, 121.
- Alpha particles from uranium**, on the ranges of the, 439; from polonium, on the number of ions produced by, 670; on the relation between the ranges of, and periods of transformation of radioactive bodies, 981.
- rays, on ionization by, 462; on the secondary rays excited by the, from polonium, 813; theory of the absorption and scattering of the, 901.
- Anderson (Prof. A.)** on the quadrant electrometer, 380; on electric currents in air at atmospheric pressure, 750.
- Andrade (Dr. E. N. da C.)** on the nature and velocity of migration of the carriers of electricity in flames containing metallic vapours, 865.
- Angle**, on the trisection of a, 646, 860, 861.
- Angular displacements**, on an instrument for measuring small, 385.
- Ashworth (Dr. J. R.)** on the magnetic temperature coefficients of the ferro-magnetic elements, 36.
- Asteroids**, on the, 337.
- Atmosphere**, on the effects of the diurnal rotation on the upper, 664; on the electrification of the, 852.
- Aurora borealis**, on the properties of the rays producing, 211.
- Barium**, on the positive thermions from salts of, 127.
- Barkla (Prof. C. G.)** on ionization in gaseous mixtures by Röntgen radiation, 317; on the absorption of X-rays and fluorescent X-ray spectra, 987.
- Barton (Prof. E. H.)** on simultaneous vibration curves for strings and air of violin, 885.
- Barus (Prof. C.)** on the rectification of the spectrum in relation to the shifts of ellipses in displacement interferometry, 942.
- Blakesley (T. H.)** on a kinematic method of finding the roots of equations, 892.
- Bohr (Dr. N.)** on the electron theory of thermoelectric phenomena, 984.
- Books**, new:—Durell's Course of Plane Geometry for Advanced Students, 445; Milne's Homogeneous Coordinates for use in Colleges and Schools, 446; Fleming's The Propagation of Electric Currents in Telephone and Telegraph Conductors, 446; Bulletin of the Bureau of Standards, 447;

- Love's Some Problems of Geodynamics, 862; Darwin's The Tides, 862; Grays' Treatise on Dynamics, 863; Barton's Analytical Mechanics, 863; U.S. Coast and Geodetic Survey, 864; Kaye and Laby's Physical and Chemical Constants, 1000.
- Bragg (Prof. W. H.) on the direct or indirect nature of the ionization by X-rays, 647.
- Bromwich (Dr. T. J. I'A.) on the trisection of an angle, 860.
- Bronson (Prof. H. L.) on the distribution of the active deposit of radium in an electric field, 714.
- Buckingham (E.) on the time-scale, 651; on the deduction of Wien's displacement law, 920.
- Burton (Dr. C. V.) on the micro-azimometer, 385.
- Burton (Prof. E. F.) on the effect of electricity on streams of water drops, 148.
- Calcium, on the positive thermions from salts of, 135.
- carbonate, on the solubility of, in water, 958.
- Callendar (Prof. H. L.) on the absolute expansion of mercury, 679; on the anisotropic expansion of a drawn tube of vitreous silica, 998.
- Campbell (Dr. N.) on delta rays, 46; on ionization by collision, 400, 986; on ionization by alpha rays, 462; on the electrical resistance of xylol-alcohol mixtures, 668; on non-Newtonian mechanics, 688.
- Carbon, on the ionization produced by, at high temperatures, 192.
- dioxide, on the recombination of ions in, 747.
- Chemical potential, on the application of the theory of, to the thermodynamical theory of solutions, 483.
- Chlorine, on the action of ultraviolet light on, 757.
- Clouds, on the effect of, on ionization, 352.
- Cobalt, on the magnetic temperature coefficients of, 36.
- Collier (V.) on the absorption of X-rays and fluorescent X-ray spectra, 987.
- Compton (K. T.) on the influence of the contact difference of potential between the plates emitting and receiving electrons liberated by ultra-violet light on the measurement of the velocities of these electrons, 579.
- Condensation nuclei, on the production of, by intense cooling and by ultraviolet light, 849.
- Conductivity, on the unilateral, of sulphated accumulator plates, 742.
- Contact electromotive forces, on, 750.
- Cosine law of radiation, on the, 237.
- Cotter (J. R.) on the trisection of an angle, 861.
- Darwin (C. G.) on the effects of the diurnal rotation on the upper atmosphere, 664; on a theory of the absorption and scattering of the α rays, 901.
- Davies (H.) on a relation between coefficients of expansion of liquids and their critical temperatures, 657.
- Davisson (C. J.) on the positive thermions from the salts of the alkaline earths, 121; on the role played by gases in the emission of positive thermions from salts, 139.
- Day (F. H.) on the absorption of Röntgen rays in air, 683.
- Delta rays, on, 46.
- Diffraction gratings with controlled groove form, on, 310.
- Displacement law, on the deduction of Wien's, 920.
- Diurnal rotation, on the effects of the, on the upper atmosphere, 664.
- Drops, on the effect of electricity on streams of water, 148; photographic measurements of pendent, 417.
- Earth, on the electrification of the surface of the, 852.
- Echelon grating, on the aberration of an, 25.
- Electric conductivity, on the unilateral, of sulphated accumulator plates, 742.
- currents in air at atmospheric pressure, on, 750.

- Electric field, on the distribution of the active deposit of radium in an, 714.
- resistance of xylol-alcohol mixtures, on the, 668.
- Electrical theory of matter, on a deduction of the effects of uniform translatory motion from the, 64.
- Electricity, on the effect of, on streams of water drops, 148; on the nature and velocity of migration of the carriers of, in flames containing metallic vapours, 865.
- Electrification of the atmosphere and surface of the earth, on the, 852.
- Electrified particles, on ionization by moving, 449.
- Electrochemistry of radioactive bodies, on the, 628.
- Electrometer, on the quadrant, 380.
- Electron theory of contact electromotive force, on the, 263.
- — of matter, some applications of the, 594.
- — of thermoelectric phenomena, on the, 984.
- Electrons, on the method of determining the motions of, 86; on contact difference of potential and the velocities of, 579; on the collisions of, in metals, 595.
- Equations, on a kinematic method of finding the roots of, 892.
- Erikson (Prof. H. A.) on the recombination of ions in carbon dioxide and hydrogen, 747.
- Eumorfopoulos (N.) on the expansion of mercury and of quartz, 653.
- Eve (Dr. A. S.) on the absorption of Röntgen rays in air, 683.
- Expansion, on a relation between coefficients of, and critical temperatures, 657.
- Fajans (Dr. K.) on the growth of radium C from radium B, 292.
- Ferguson (A.), photographic measurements of pendent drops, 417.
- Ferromagnetic elements, on the magnetic temperature coefficients of the, 36.
- Filon (Prof. L. N. G.) on the investigation of stresses in a rectangular bar by means of polarized light, 1.
- FitzGerald Lorentz contraction, on the, 86.
- Flames, on the nature and velocity of migration of the carriers of electricity in, 865.
- Fletcher (A. L.) on the radium content of secondary rocks, 279.
- Fresnel's laws of reflexion, on departures from, 431.
- Gamma radiation from radium B, on, 302.
- Gas molecules, on selective reflexion, scattering and absorption by resonating, 689.
- Gaseous jets, on the instability of, 368.
- mixtures, on ionization in, by Röntgen radiation, 317.
- Gases, on the role played by, in the emission of positive thermions from salts, 139; on opalescence of, in the critical state, 165; on a method of investigating the transpiration of, through tubes, 250.
- Geiger (Dr. H.) on the ranges of the α particles from uranium, 439.
- Gill (E. W. B.) on the variation with distance of the ionization produced by Röntgen rays, 114; on ionization by collision in helium, 837.
- Gratings, on the aberration of echelon, 25; on diffraction with controlled groove form, 310.
- Harmonic motions, on the composition of two simple, 977.
- Helium, on ionization by collision in, 837.
- Heuse (W.) on the thermal expansion of mercury, 412.
- Hevesy (Dr. G. v.) on the electrochemistry of radioactive bodies, 628.
- Hudson (Miss H. P.) on the trisection of an angle, 860.
- Huntington (Prof. E. V.) on a new approach to the theory of relativity, 494.
- Hydrogen, on the charges of thermions produced in, 173; on the recombination of ions in, 747.
- Induction, on unipolar, 937.
- Interferometry, on the rectification of the spectrum in relation to the shift of ellipses in, 942.

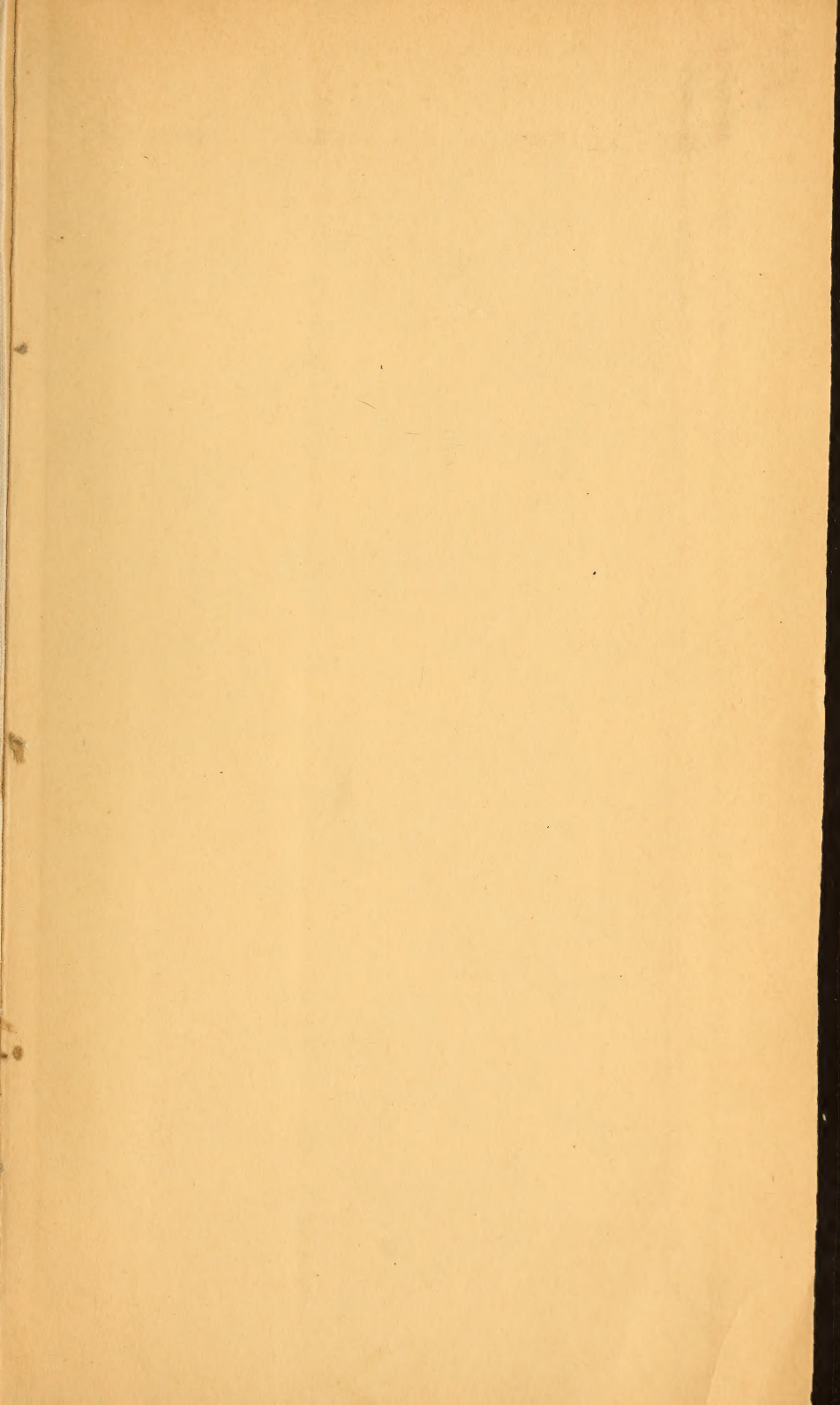
- Ionization produced by Röntgen rays, on the variation with distance of the, 114; on the, produced by carbon at high temperatures, 192; on, in gaseous mixtures by Röntgen radiation, 317; on the effect of clouds on, 352; on, by collision, 400, 856, 986; on, by moving electrified particles, 449; on, by α rays, 462; on the nature of the, by X-rays, 647; on, by collision in helium, 837.
- Ions, on the virial of a mixture of, 551; on the number of, produced by an α particle from polonium, 670; on the charges on, 677; on the recombination of, in carbon dioxide and hydrogen, 747.
- Iron, on the magnetic temperature coefficients of, 36.
- Jets, on the instability of gaseous, 368.
- Joly (Prof. J.) on the radioactivity of the rocks of the St. Gothard tunnel, 201.
- Jones (Prof. H. C.) on absorption spectra and the solvate theory of solution, 730.
- Kendall (J.) on the solubility of calcium carbonate in water, 958.
- Kennard (E. H.) on unipolar induction, 937.
- Kilby (W. B.) on simultaneous vibration curves for strings and air of violin, 885.
- Kinematic method of finding the roots of equations, on a, 892.
- King (L. V.) on the cosine law of radiation, 237; on absorption problems in radioactivity, 242.
- Kleeman (Dr. R. D.) on the law of molecular attraction, 656.
- Kuenen (Prof. J. P.) on the deduction of thermodynamical relations, 752.
- Light, on the investigation of stresses by means of polarized, 1; on selective reflexion, scattering and absorption of, by resonating gas molecules, 689; on the action of ultraviolet, on chlorine, 757; on the production of condensation nuclei by ultraviolet, 849.
- Liquids, on the viscosity of, 458; on a relation between coefficients of expansion of, and their critical temperatures, 657; on the internal pressure of, 955.
- Lowell (Prof. P.) on the asteroids, 337.
- Ludlam (Dr. E. B.) on the action of ultraviolet light on chlorine, 757.
- Lunnon (R. G.) on the unilateral conductivity of sulphated accumulator plates, 742.
- Lyle (Prof. T. R.) on harmonic analysis, 334.
- McLaren (S. B.) on the emission and absorption of radiation, 513.
- Magnesium, on the spectrum of the, arc, 94; on the positive thermions from salts of, 136.
- Magnetic temperature coefficients of the ferromagnetic elements, on the, 36.
- Makower (Dr. W.) on the growth of radium C from radium B, 292; on γ radiation from radium B, 302.
- Maskelyne (N.) on the trisection of an angle, 646.
- Meigh (E.) on the instability of gaseous jets, 368.
- Mercury, on the thermal expansion of, 412, 653, 679; on the viscosity of, 458.
- Metal films, on the photoelectric properties of thin, 542.
- Metallic vapours, on the nature and velocity of migration of the carriers of electricity in flames containing, 865.
- Micro-azimometer, on the, 385.
- Milner (Dr. S. R.) on the virial of a mixture of ions, 551.
- Molecular attraction, on the law of, 101, 656.
- Morrison (H. N.) on electric currents in air at atmospheric pressure, 750.
- Moseley (H. G. J.) on γ radiation from radium B, 302.
- Motion, on a deduction of the effects of uniform translatory, from the electrical theory of matter, 64.
- Moving body, on the mass of a, 375.
- Nicholson (Dr. J. W.) on the α particle, 333.
- Nickel, on the magnetic temperature coefficients of, 36.
- Non-Newtonian mechanics, on, 375, 688.
- Nuttall (J. M.) on the ranges of the α particles from uranium, 439.

- O'Connor (Miss E.) on the spectrum of the magnesium high-frequency arc, 94.
- Opalescence of gases in the critical state, on, 165.
- Orangite, on the rate of evolution of heat by, 183.
- Osmotic pressure, on the vapour-pressure theory of, 486.
- Owen (Dr. G.) on the effect of clouds on ionization, 352.
- Parker (A.) on the ionization produced by carbon at high temperatures, 192.
- Photoelectric fatigue, on, 255; properties of thin metal films, on the, 542; phenomena, on, 615.
- Pidduck (F. B.) on ionization by collision in helium, 837.
- Polarized light, on the investigation of stresses by means of, 1.
- Polonium, on the number of ions produced by an α particle from, 670; on the secondary rays excited by the alpha rays from, 813.
- Pomeroy (J. C.) on the charges on thermions produced in air and hydrogen at atmospheric pressure, 173.
- Poole (H. H.) on the rate of evolution of heat by orangite, 183.
- Porter (Prof. A. W.) on the viscosity of liquids, 458.
- Potential, on the application of the theory of chemical, to the thermodynamical theory of solutions, 483; on contact difference of, and the velocities of electrons, 579.
- Pound (V. E.) on the secondary rays excited by the alpha rays from polonium, 813.
- Pring (Dr. J. N.) on the ionization produced by carbon at high temperatures, 192.
- Quadrant electrometer, on the, 380.
- Quartz, on the thermal expansion of, 653.
- Quaternionic form of relativity, on the, 790.
- Radiation, on the cosine law of, 237; on the emission and absorption of, 513.
- Radioactive bodies, on the electrochemistry of, 628; on the relation between the ranges of α particles and the periods of transformation of, 981.
- Radioactivity, on the, of the rocks of the St. Gothard tunnel, 201; on absorption problems in, 242.
- Radium, on the distribution of the active deposit of, in an electric field, 714.
- A, on γ radiation from, 302.
- C, on the growth of, from radium B, 292.
- content of secondary rocks, on the, 279.
- Ramsauer (Dr. C.) on the production of condensation nuclei in air and in vapours by intense cooling and by ultraviolet light, 849.
- Rayleigh (Lord) on departures from Fresnel's laws of reflexion, 431.
- Reflexion, on departures from Fresnel's laws of, 431; on selective, by resonating gas molecules, 689.
- Reinganum (Prof. M.) on a relation between the atomic volume and spectra of elements, 336.
- Relativity, on a new approach to the theory of, 494; on the quaternionic form of, 790.
- Richardson (Prof. O. W.) on the electron theory of contact electromotive force and thermoelectricity, 263; on some applications of the electron theory of matter, 594.
- Roberts (J. H. T.) on a method of investigating the transpiration of gases through tubes, 250; on the effect of clouds on ionization, 352; on the instability of gaseous jets, 368; on transverse vibrations of a string maintained by forces of double frequency, 931.
- Robinson (Dr. J.) on photoelectric fatigue, 255; on photoelectric properties of thin metal films, 542.
- Rocks, on the radioactivity of the, of the St. Gothard tunnel, 201; on the radium content of secondary, 279.
- Röntgen rays, on the variation with distance of the ionization produced by, 114; on ionization in gaseous mixtures by, 317; on the nature of the ionization by, 647; on the absorption of, in air, 683; on the absorption of, and fluorescent spectra of, 987.
- Rotation, on the effects of the diurnal, on the upper atmosphere, 664.

- Rudge (Prof. W. A. D.) on the electrification of the atmosphere and surface of the earth, 852.
- St. Gothard tunnel, on the radio-activity of the rocks of the, 201.
- Scheel (K.) on the thermal expansion of mercury, 412.
- Searle (J. H. C.) on the problem of the weir, 772.
- Shorter (S. A.) on the application of the theory of chemical potential to the thermodynamical theory of solutions, 483.
- Silberstein (Dr. L.) on the quaternionic form of relativity, 790.
- Silica, on the anisotropic expansion of a drawn tube of vitreous, 998.
- Simons (L.) on ionization in gaseous mixtures by Röntgen radiation, 317.
- Smoluchowski (Prof. M. S.) on opalescence of gases in the critical state, 165.
- Solutions, on the application of the theory of chemical potential to the thermodynamical theory of, 483; on absorption spectra and the solvate theory of, 730.
- Spectra, on changes in diffraction, produced by aberration, 25; on absorption, and the solvate theory of solution, 730.
- Spectral series, on the theory of, 660.
- Spectrum, on the, of the magnesium high-frequency arc, 94; on the rectification of the, in relation to the shift of ellipses in interferometry, 942.
- Stansfield (Dr. H.) on changes in diffraction spectra produced by aberration and the aberration of an echelon grating, 25.
- Stephenson (A.) on the propagation of periodic æther disturbance, 809.
- Steven (A. I.) on the composition of two simple harmonic motions exhibited by a stretched string, 977.
- Stresses in a bar, on the investigation of, by means of polarized light, 1.
- String, on transverse vibrations of a, maintained by forces of double frequency, 931; on the composition of two simple harmonic motions exhibited by a stretched, 977.
- Strontium, on the positive thermions from salts of, 132.
- Sukhodski (W.) on the internal pressure of a liquid, 955.
- Swann (Dr. W. F. G.) on a deduction of the effects of uniform translatory motion from the electrical theory of matter, 64; on the FitzGerald Lorentz contraction and the method of determining the motions of electrons, 86.
- Taylor (Dr. T. S.) on the number of ions produced by an α particle from polonium, 670.
- Thermions, on the positive, from the salts of the alkaline earths, 121; on the role played by gases in the emission of positive, from salts, 139; on the charges on, produced in air and hydrogen at atmospheric pressure, 173.
- Thermodynamical relations, on the deduction of, 752.
- Thermoelectric phenomena, on the electron theory of, 984.
- Thermoelectricity, on the electron theory of contact electromotive force and, 263.
- Thompson (Prof. S. P.) on harmonic analysis, 334.
- Thomson (Sir J. J.) on ionization by moving electrified particles, 449.
- Time-scale, on the, 651.
- Tolman (Prof. R. C.) on non-Newtonian mechanics, 375.
- Townsend (Prof. J. S.) on the charges on ions, 677; on ionization by collision, 856.
- Transpiration of gases through tubes, on a method of investigating the, 250.
- Tyrer (D.) on the law of molecular attraction, 101.
- Ultraviolet light, on the action of, on chlorine, 757; on the production of condensation nuclei by, 849.
- Unipolar induction, on, 937.
- Uranium, on the ranges of the α particles from, 439.
- Vapour-pressure, on the effect of pressure on, 485.
- Vegard (L.) on the properties of the rays producing aurora borealis, 211.
- Vibrations, on transverse, of a string maintained by forces of double frequency, 931.
- Violin, on simultaneous vibration curves for strings and air of, 885.

- Virial of a mixture of ions, on the, 551.
- Viscosity, on the, of liquids, 458.
- Walmsley (H. P.) on changes in diffraction spectra produced by aberration and the aberration of an échelon grating, 25.
- Water, on the viscosity of, 458.
- drops, on the effect of electricity on streams of, 148.
- Weir, on the problem of the, 772.
- Wellisch (Prof. E. M.) on the distribution of the active deposit of radium in an electric field, 714.
- Wiegand (W. B.) on the effect of electricity on streams of water drops, 148.
- Wien's displacement law, on the deduction of, 920.
- Wilson (Prof. H. A.) on the theory of spectral series, 660; on the relation between the ranges of α particles and the periods of transformation of radioactive bodies, 981.
- Wood (Prof. R. W.) on diffraction gratings with controlled groove form and abnormal distribution of intensity, 310; on selective reflexion, scattering, and absorption by resonating gas molecules, 689.
- X-rays, on the absorption of, and fluorescent X-ray spectra, 987.
- Xylol-alcohol mixtures, on the electrical resistance of, 668.

END OF THE TWENTY-THIRD VOLUME.





SMITHSONIAN INSTITUTION LIBRARIES



3 9088 01202 4899